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Environmental Assessment for Residual Oil Utilization
Second Annual Report

Catalytic, Inc, Charlotte, NC

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Industrial Environmental Research Lab, Research Triangle Park, NC

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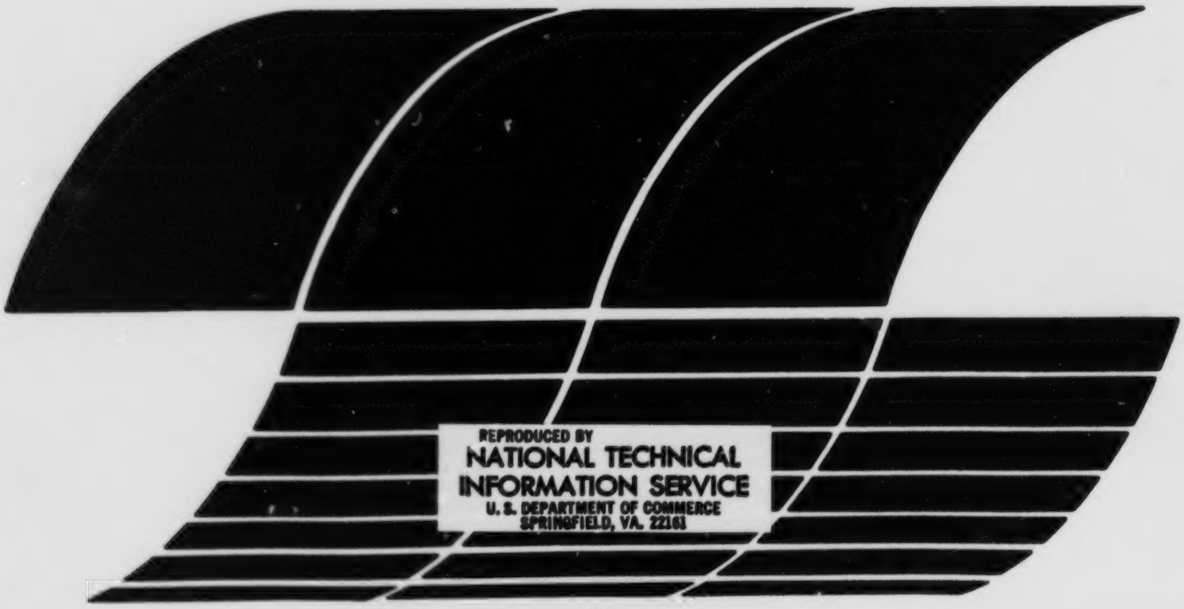
Interagency Energy/Environment R&D Program Report



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16. ABSTRACT The report describes progress in an environmental assessment of processes utilizing residual oil for electric power generation. It explains the methodology of environmental assessment and reports major progress in the areas of: current progress technology, current environmental background and objectives development, data acquisition, control technology assessment, and environmental alternatives analysis. It presents emissions data from the literature and preliminary sampling, with material balances and flow diagrams for hydrodesulfurization, flue gas desulfurization, partial oxidation, and chemically active fluid bed processes. It describes a computer program for a theoretical engineering analysis that will provide emissions output for the processes studied. A detailed sampling and analysis matrix has been developed that specifies sampling points, procedures, and analyses, including bioassays for all emissions and effluents. Multimedia Environmental Goals (MEGs) and Minimum Acute Toxicity Effluents (MATEs) are used to develop pollutant prioritization and source analysis models. Methods for developing economic cost models are described. Future plans include sampling of field installations, SAM/IA analysis of emissions and effluent data, economic and energy efficiency analysis, describing areas for furthur research and development, and databases for standards and engineering design.

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Assessments	Oxidation	Stationary Sources	14B	07B,07C
Residual Oils	Fluidized Bed Processing	Environmental Assessment	21D	13H
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by

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SECTION 1
EXECUTIVE SUMMARY

1.1 INTRODUCTION

Catalytic, Inc. is making a three-year world-wide study for EPA on the use of residual fuel oil. This study includes environmental evaluation and related economics, efficiencies, and systems analyses. The processes being studied are:

- Hydrodesulfurization (HDS)/Hydrodenitrogenation (HDN)
  - Gulf HDS
  - UOP Residual Desulfurization
  - Exxon Residfining

- Partial Oxidation (POX)
  - Texaco synthesis gas generation
  - Shell gasification
  - Esso Chemically Active Fluid Bed Process (CAFB)

- Combined Cycle
  - Gas turbine on residual fuel oil
  - Gas turbine on synthesis gas from POX
  - Flue Gas Desulfurization (FGD)
  - Non-regenerable
  - Regenerable

The HDS units produce a clean, low sulfur residual fuel oil. The POX units give a low sulfur, low Btu fuel gas, consisting mainly of H_2 and CO plus some CO_2. They can be operated either with oxygen or air for gasification. The CAFB pilot unit at Abingdon, England, is being covered, as well as the CAFB unit designed by Foster Wheeler for Central Power and Light in San Benito, Texas. In this process, the residual fuel oil is partially oxidized with air and the resulting low sulfur gas is burned in a boiler. The fluidized limestone bed, containing sulfur, metals, and ash, is partially regenerated and returned to the unit. A combined cycle unit, using POX feed, is being designed by Beard Engineering of Baton Rouge, La., for the Louisiana Municipal Power Commission (LAMPCO).

The study of commercial operating units and demonstration units is presented in this second annual report.

1.2 OBJECTIVES AND SCOPE OF WORK

This report summarizes the results of the second year of the "Environmental Assessment for Residual Oil Utilization." The "Environmental Assessment for Residual Oil Utilization" for the production of electricity by utility industry is a three year program to: (1) review and analyze the existing environmental, engineering, and cost data; (2) identify important pollutants and project attainable emission levels; (3) identify missing information and design a program(s) to develop such information; and (4) design and conduct source sampling, fugitive emissions, and ambient monitoring program(s). The program covers boiler and combined cycle turbine fuel and pipeline gas manufactured from residual oil. Those flue gas scrubbers operating on residual oil-fired boilers have also been studied. This is part of a multi-project program directed toward attaining and maintaining current and projected environmental quality standards to the year 2000.

During the second program year, the apparent need for a consistent evaluation and reliable comparison of combustion fuels and processes led to the initiation of an environmental assessment methodology by EPA. In support of the new environmental assessment program methodology, Catalytic has planned extensive additional work for the assessment of residual oil processing and combustion. Examples of the work being planned are: the preparation of interim assessment documents for program activities, the preparation of interim assessment reports by process types, annual reports of current and planned activities for standards support, and an expansion of the sampling and analytical efforts to satisfy the methodology requirements for a consistent data base.

The objective of the work reported here is to define the problems and justify the environmental goals of residual oil utilization through a comprehensive environmental and engineering analysis. The overall emission control goals for each process category under study shall, at a minimum, meet the existing standards of performance for fossil-fired steam generators. The processes under study are all considered economically feasible, compatible with boiler design in the utility industry, and environmentally sound. The primary objective, then, of this environmental assessment program is to assure that an adequate research data base is available to support the development of standards and guidelines established by EPA. A simplified block flow diagram shown in Figure 1-1 gives the relationship between the steps of environmental assessment and control technology development. The environmental assessment goals for this program are as follows:

1. Determine the emissions loadings for all pollutants in all media;
2. Determine control costs;
3. Explore all applicable, existing, and future control and disposal options;
4. Compare emissions loadings with existing standards, estimated multimedia environmental goals, and bioassay specifications; and
5. Rank the control options, evaluate environmental effectiveness, and determine the problems and needs for research and development.

1.3 PROGRAM OVERVIEW

The body of this report is organized according to the five environmental assessment elements shown in Figure 1-1. The activities performed by Catalytic, Inc. in the residual oil study are indicated on the figure. In this environmental assessment study, Catalytic is coordinating with other EPA contractors who are providing information on other environmental assessment activities. A brief description of each of these five steps follows.

Current Process Background

This section includes a brief description of the residual oil utilization processes, the development schedules and status, the input for developing acquisition of environmental data, and the potential for national and/or regional

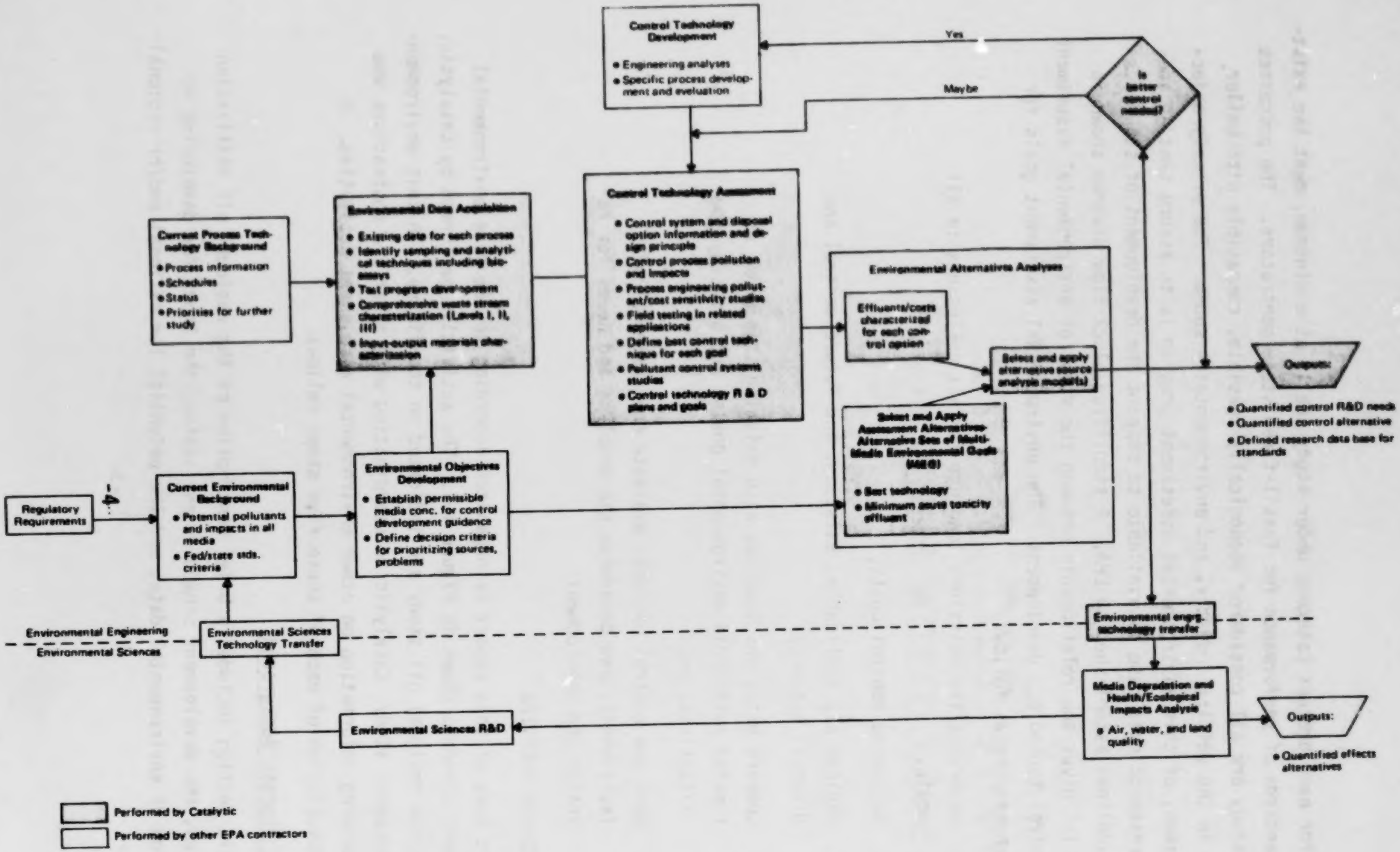
Control Technology Development
• Engineering analyses
• Specific process development and evaluation
Yes
Maybe
Is better control needed?
Current Process Technology Background
• Process information
• Schedules
• Status
• Priorities for further study
Environmental Data Acquisition
• Existing data for each process
• Identify sampling and analytical techniques including bioassays
• Test program development
• Comprehensive waste stream characterization (Levels I, II, III)
• Input-output materials characterization
Control Technology Assessment
• Control system and disposal option information and design principle
• Control process pollution and impacts
• Process engineering pollutant/cost sensitivity studies
• Field testing in related applications
• Define best control technique for each goal
• Pollutant control systems studies
• Control technology R & D plans and goals
Environmental Alternatives Analyses
Effluents/costs characterized for each control option
Select and apply alternative source analysis model(s)
Select and Apply Assessment Alternatives-Alternative Sets of Multi-Media Environmental Goals (MEG)
• Best technology
• Minimum acute toxicity effluent
Outputs:
• Quantified control R&D needs
• Quantified control alternative
• Defined research data base for standards
Regulatory Requirements
Current Environmental Background
• Potential pollutants and impacts in all media
• Fed/state stds. criteria
Environmental Objectives Development
• Establish permissible media conc. for control development guidance
• Define decision criteria for prioritizing sources, problems
Environmental Engineering
Environmental Sciences
Environmental Sciences Technology Transfer
Environmental engrg. technology transfer
Media Degradation and Health/Ecological Impacts Analysis
• Air, water, and land quality
Outputs:
• Quantified effects alternatives
Environmental Sciences R&D
Performed by Catalytic
Performed by other EPA contractors

Figure 1-1 Environmental Assessment/Control Technology Development Diagram

use. This step will be used to define the current control costs on existing residual oil processes. Economic cost data will be helpful in assessing the economic feasibility of existing process control technology for the utility industry.

The environmental goals for non-regenerable FGD processes must be based on Japanese units, because all U. S. technology in this area is based on coal. The most serious problem with non-regenerable FGD processes is related to the disposal of sulfur containing waste materials. The sludge producing systems require solids disposal techniques and use large areas of land. In the U. S., it is not likely that a cost credit may be taken for gypsum or other sludges from non-regenerable FGD processes. The regenerable FGD processes generally require much more auxiliary energy than non-regenerable types, and by-product sulfur must be recovered in a usable, marketable form. Emissions goals for auxiliary sulfur recovery processes must be carefully studied because of the variable feed streams compositions from the regenerable FGD scrubbers. A serious problem associated with MgO regenerable scrubbers is the fugitive loss of fine sorbent, which is inherent to this process.

Without serious environmental consequences, catalytic hydrodesulfurization of residual oil can effectively reduce the sulfur and heavy metal content to desirable levels required for direct combustion. However, an assessment of the final disposal and regeneration of spent catalysts is necessary to provide a total view of the fate of important potential pollutants. These pollutants are generally thought to be carried from the HDS processes with the spent catalyst. Economic costs are the major stumbling block which limit the potential for immediate use of HDS processes. The high cost of hydrogen and high initial investment for HDS processes are limiting its full developmental potential. The major environmental problem with POX processes is the necessity for purging of carbon soot by-product which contains a high concentration of the heavy metals in residual oil. The cost of oxygen needed for making medium Btu (325 Btu/scf) gas with the POX process limits its development.

The CAFB process in the demonstration stage shows promise for being an excellent advanced cleanup technique with minimal environmental effluent problems using residual oil. However, further development is needed to collect sorbent fines prior to combustion and to assess disposal methods for spent bed materials.

Current Environmental Background

This environmental assessment step will be used to summarize key regulations and to document existing effluent standards, which will be compared with emissions loadings. This step will be useful in identifying control needs for major pollutant problem areas. It is very important that advanced technologies, when commercially applied, do not possess their own set of environmental problems. The major reason for summarizing effluent standards is to identify and help avoid potential environmental problems that may be associated with promising technologies. Thus, it is necessary to make a complete environmental characterization of newly-developing technologies.

Environmental objectives development has been used in amplifying goals for all possible effluents based on health standards. Recently, there has been a significant expansion in EPA responsibility because of the new Toxic Substances Control Act. This Act is concerned not only with the effluents from the manufacture of hazardous chemicals, but also with the processing of all chemicals. The primary efforts in environmental objectives development have been focused on protecting human health, ecological systems, and minimizing the associated risks.

Environmental Data Acquisition

This step will be used to determine emissions loadings by projecting possible emissions of compounds based on theoretical calculations and engineering considerations. It is anticipated that a comprehensive source sampling program will be undertaken to develop the emissions data base necessary for supporting environmental standards and guidelines and to provide the actual emissions information necessary for comparison with effluent goals. In some cases, an ambient monitoring program may also be needed.

In order to compare the projected emissions loadings for each residual oil utilization process, a composite analysis was developed based on all input streams, e.g., residual oil and limestone. Theoretical engineering analyses were then conducted to serve as a check on the empirical data obtained from actual sampling. Limited baseline emissions data were projected based on analyses of grab samples taken from commercial residual oil units. Finally, a test program was developed for the sampling and analysis of each residual oil utilization process. A sampling/analysis matrix was constructed to ensure collection of all streams based on Level 1 and Level 2 environmental assessment protocol.

Control Technology Assessment

The Multimedia Environmental Control Engineering Handbook (MECEH) categorizes all commercially-available control technologies, provides technical data for each process, and includes a list of known suppliers that manufacture the specific equipment or license the technology. The control processes categorized in the MECEH include: (1) gas treatment, (2) liquids treatment, (3) solids treatment, (4) final disposal, (5) process modifications, (6) combustion modification, (7) fuel cleaning, (8) fugitive emissions control (to be performed later), and (9) accidental release technology (to be performed later).

In this step, applicable, existing, and future control/disposal options for residual oil usage were explored. For the purpose of this environmental assessment program, environmental control technology options have been divided into four areas. The numbers in parenthesis below illustrate the specific device or process describing the classification, generic device, design type, and each specific device in that category.

Modification of Process Operating and Design Conditions--

(5.0)	Process modifications on CAFB
(5.1)	Feedstock changes; residual oils, bitumen, lignite, limestone
(5.3)	Process design improvements in CAFB burners

Pretreatment of Input Streams--

(7.)	Fuel cleaning
(7.4)	Treatment of liquid fuels
(7.4.1.1)	Demex
(7.4.2)	Hydrotreating
(7.4.2.4)	Resid HDS (Gulf)
(7.4.2.10)	HDN (Engelhard)

(7.4.2.26)	Residual oil HDS (Shell)
(7.3.1.5)	Krupp, Lurgi; Retort (POX)

Use of Add-on Control Devices--

(1)	Gas treatment
(1.4)	Liquid scrubbers/contactors
(1.4.1)	Absorption processes
(1.4.1.9)	Cyclic lime process - FGD
(1.4.1.14)	Magnesium oxide absorption
(1.4.6.13)	Multiventuri scrubber
(1.7.2.6)	Claus/partial combustion
(1.8.1.1)	Catalytic removal of NO_x

Minimization of the Impact of Solid Residue Disposal--

(3.0)	Solids treatment
(3.1)	Fixation
(4.0)	Final disposal
(4.3)	Burial and landfill

Potential control techniques for residual oil process effluents were summarized and related to the technical problems and environmental needs based on discharge stream sources. An economic cost model was developed for use as a basis for comparing the economic feasibility or cost effectiveness of various processes.

Environmental Alternatives Analysis

This step shall identify the best combination of control options for residual oil utilization process variations. As an example, new process technologies, such as the chemically active fluidized bed process, will be compared with lime and limestone flue gas desulfurization, hydrodesulfurization and other gasification processes. In this step, the pollutant removal capabilities will be compared; and, the possible pollutant control achievable will be compared with other existing control technologies. Auxiliary power and process water requirements will be compared, as well as input fuel variations and control technology problems. This analysis will be used to rank the control technologies, to evaluate the environmental effectiveness, and to identify pollution control problems and needs for further research and development.

SECTION 2

CURRENT PROCESS TECHNOLOGY

This section presents an update to the "Process Technology Background for Environmental Assessment/Systems Analysis Utilizing Residual Fuel Oil," which was prepared for the EPA by Catalytic, Inc., as the first annual report under this program. The residual oil utilization processes discussed here include Phase I processes, which are operating or in commercial design, and Phase II processes, which are in demonstration plant design. Attention has been given to non-regenerable flue gas desulfurization, regenerable flue gas desulfurization, hydrodesulfurization/hydrodenitrification, partial oxidation, and the chemically active fluid bed process. For each process category, information is given pertaining to the system description, raw materials, products, and discharge streams. In addition, the process status gives updated costs, energy efficiencies, applicability, and the size and number of units now planned or in operation. Priorities for further study are to include Phase III processes, which are in the pilot plant phase of development, and to update existing process information as further sampling and analysis studies are used to develop missing data.

2.1 NON-REGENERABLE FLUE GAS DESULFURIZATION

Process Information

Flue gas desulfurization processes (FGD) may be classified by end product as regenerable, whereby sulfur from the oil is recovered in a usable, marketable form, or non-regenerable, requiring the disposal of the sulfur as a non-recoverable waste material.

Information from Catalytic's information-gathering trip to Japan will be relied upon to arrive at meaningful data to assess the FGD process. There have been some domestic FGD units using oil in the recent past, but the current U. S. technology for flue gas scrubbing is now concerned with coal-fired plants (Table 2-1). The technology for coal-fired FGD is very similar to that for oil fired; but, in general, this discussion is based on Catalytic's Japanese trip and information from ongoing contact with the Japanese. The great majority of FGD units in Japan clean the flue gas from residual oil-fired boilers (Table 2-2). Both tables show that lime and limestone systems are by far the most common types of the operating FGD processes.

The limestone FGD process was selected as most representative of the non-regenerable FGD chemical process types. A typical flow diagram for this process is shown on Figure 2-1. Boiler stack gas is washed in a two-stage (venturi and absorber) scrubber system with a recirculating slurry (pH of 5.8-6.4) of limestone and reacted calcium salts in water. The overall absorption reaction taking place in the scrubber and the hold tanks produces hydrated calcium sulfite:

$$CaCO_3 + SO_2 + \tfrac{1}{2} H_2O \longrightarrow CaSO_3 \cdot \tfrac{1}{2} H_2O + CO_2$$

In practice, some of the absorbed SO_2 is oxidized by oxygen, which is also absorbed from the flue gas. This shows up in the slurry as either gypsum ($CaSO_4 \cdot 2H_2O$) or as a calcium sulfite/sulfate mixed crystal $[Ca(SO_3)_x(SO_4)_y \cdot zH_2O]$. Slurry is recycled around the scrubber to obtain the high liquid-to-gas ratios required.

The desulfurized flue gas passes through a demister and, prior to discharge to the atmosphere, is reheated to achieve buoyancy and raise gas temperature above the dew point. Limestone feed is ground wet prior to addition to the scrubber effluent hold tank. Calcium sulfite and sulfate salts are withdrawn to a disposal area for discard.

Process advantages and disadvantages were described in our previous annual report. A considerable quantity of $CaSO_3/CaSO_4$ solid waste is generated, approaching as much as four times the weight of the sulfur removed. Wastes discharged to settling ponds often have poor settling properties, which may lead to difficulty when reclaiming the land for future use. Potential runoff from the ponding site could lead to additional water pollution problems due to the high make-up water and high waste water flows. Another disadvantage of the limestone slurry process has been low operating reliability from slurry plugging of scrubber internals. Also, reheat and high pressure drop cause an increase in the already high energy consumption. One advantage of the process is

TABLE 2-1. FGD SERVICE IN THE UNITED STATES

	FGD Capacity, MW_e			
Process	Operational	Construction	Planning	Total
Limestone	4,047	6,470	7,486	18,003
Lime	4,237	3,773	5,942	13,952
Lime/limestone	20	0	0	20
Sodium carbonate	375	0	634	1,009
Magnesium oxide	120	0	726	846
Wellman Lord	115	715	180	1,010
Double alkali	0	852	250	1,102
Aqueous carbonate	0	0	100	100
Totals (in MW_e)	8,914	11,810	15,318	36,042

Source: Bernard A. Laseke and Timothy W. Devitt, "Status of Flue Gas Desulfurization Systems in the United States," Flue Gas Desulfurization Symposium, Hollywood, Florida, November 8-11, 1977.

TABLE 2-2. FGD SERVICE IN JAPAN

Process	Units in Operation-1977	Flue Gas Rate-1000Nm^3/h[a]
Wet Lime & Limestone	94	40,181
Double Alkali	46	13,392
Sodium Scrubbing	335	19,961
Regenerable	30	11,537
TOTALS	505	84,891

[a] 3000Nm^3/h corresponds roughly to 1 MW$_e$. Approximately one-half of the capacity is for utility boilers, and the rest from industrial boilers and other sources such as sulfuric acid and iron ore sintering plants.

Source: Jumpei Ando and B. A. Laseke, SO$_2$ Abatement for Stationary Sources in Japan, EPA-600/7-77-103a, September 1977.

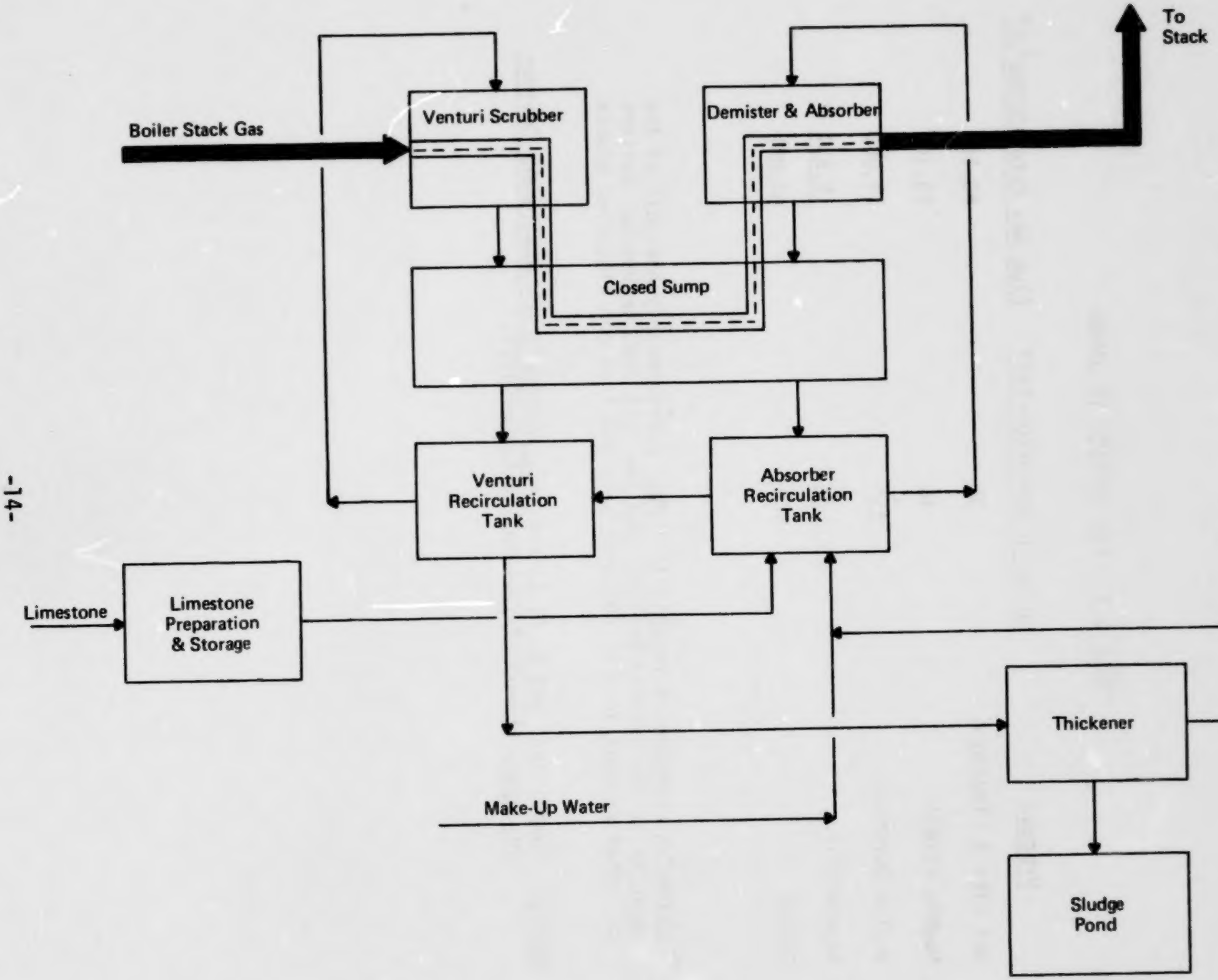

Figure 2-1 - Flow Diagram for a Typical Limestone FGD Process

a high particulate removal; efficiencies of 80% and higher are typical.

A material balance for a limestone slurry FGD system has been scaled up from typical data to reflect the process for a 500 MW_e oil-fired unit (Figure 2-2). A heat rate of approximately 10.92 kJ/W-h (10,350 Btu/kW-h) was assumed.

The combustion of residual oil with atmospheric air is used in a conventional boiler to generate steam for power generation. The products of combustion form the boiler stack gas which contains essentially all of the sulfur from the oil in the form of SO_2 and SO_3 gases, sulfate mist, and sulfates in the particulate matter. In the FGD system, the boiler stack gas is contacted by the water-limestone slurry which removes most of the SO_2/SO_3 and much of the particulate. The reheated, SO_2-reduced, stack gas is then returned to the boiler stack for release to the atmosphere. Calcium sulfite/sulfate is bled from the venturi recirculation tank and pumped to a thickener where most of the water is removed and returned to the absorber recirculation tank. The concentrated sludge is transferred to a sludge pond. Make-up water and limestone are required to balance the sludge effluent and evaporation losses, including water carried off with the clean stack gas. Detailed descriptions of the streams mentioned above were included in the first annual report.

Process Status

Updated investment and operating costs from the first annual report are shown in Table 2-3.

A recent detailed study was conducted by Ebasco Services, Inc.[4] Investment costs for limestone FGD systems are shown in Table 2-4. Operating costs were derived assuming the following:

1. 600 MW_e unit burning high sulfur Eastern coal
2. 1977 operation with 30-year levelizing period
3. Fixed Charge Rate of 18% per year
4. $375 per kilowatt capability charge (see glossary)
5. Power cost - 25 mills per kilowatt hour
6. Limestone cost - $12 per ton (997 kg) delivered
7. Maintenance cost - 3% per year on investment.

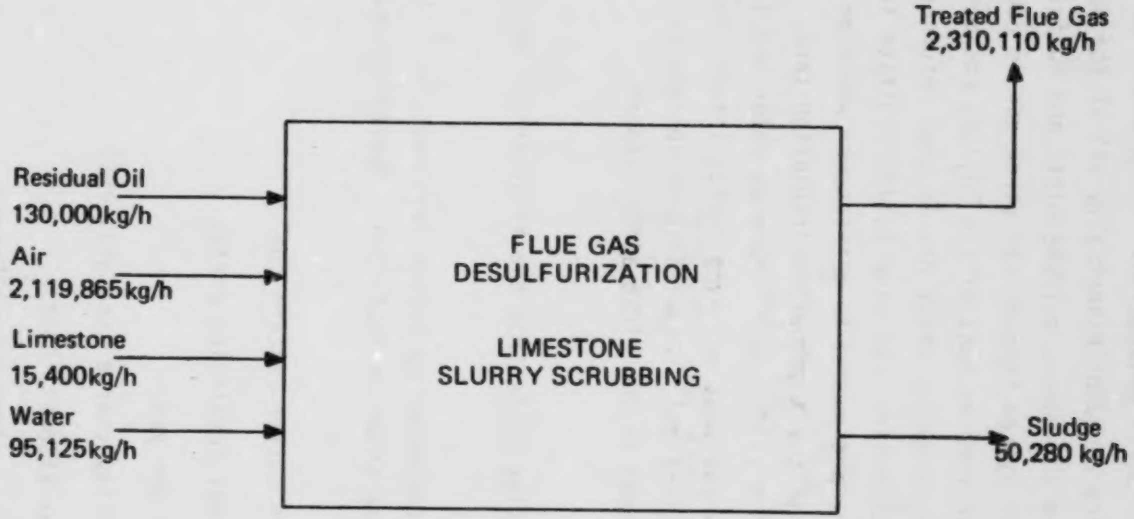

Figure 2-2 - Typical Limestone FGD Material Balance for 500 MWe Unit

TABLE 2-3. CAPITAL INVESTMENT AND ANNUAL COSTS FOR FGD PROCESSES IN THE U. S.

Power Size: 500 MW_e

Residual Oil (No. 6) = 4.0% Sulfur

Mid-1978 Battery Limits Costs

	Process	Total Capital Investment $/KW	Annual Costs Mills/kWh (No Credits)
1.	Limestone/Sludge (CaO, $CaCO_3$)	103.73	4.87
2.	Lime/Sludge ($Ca(OH)_2$)	98.01	5.06
3.	Magox/Sulfur * (MgO)	106.87	5.05
4.	Alum/Basic $Al_2(SO_4)_3$	142.89	5.58
5.	Sodium/Sulfur * (Na_2SO_3, $NaOH$, Na_2CO_3)	125.58	5.67
6.	Double Alkali/Sludge (Na_2SO_3 + $CaCO_3$ or $Ca(OH)_2$, $(NH_4)_2SO_4$ + $CaCO_3$, $Al_2(SO_4)_3$ + $CaCO_3$)	98.24	4.48
7.	Ammonia/Sulfur *	117.29	4.56
8.	Copper Oxide	156.60	5.99
9.	Citrate	117.55	5.68
10.	Activated Carbon	174.67	5.70

* Elemental Sulfur is By-product.

Source: Catalytic, Inc., "Process Technology Background for Environmental Assessment/System Analysis Utilizing Fuel Oil," 68-02-2155, EPA-600/7-77-081, August, 1977.

TABLE 2-4. MODULAR INVESTMENT COSTS FOR LIMESTONE FGD

Components	Plant Size 400 MW_e	 600 MW_e
SO_2 Removal Equipment	\$94/KW (16.4%)	\$87/KW (16.4%)
Waste Disposal Ponds	\$25/KW (4.4%)	\$14/KW (3.4%)
Waste Disposal Equipment	\$15/KW (2.6%)	\$13/KW (2.5%)
Limestone Preparation Equipment	\$14/KW (2.4%)	\$10/KW (1.9%)
	\$148/KW (25.8%)	\$128/KW (24.2%)

Notes: (1) Percentage of total plant investment is given in parentheses. Basis is high sulfur Eastern coal - no precipitator costs included.

(2) Costs are in 1977 U. S. dollars.

Source: R. L. Andrews, "Current Assessment of Flue Gas Desulfurization Technology," Combustion, XLIX, No. 9 (October 1977), 20-25.

8. Operator Labor - \$18 per hour, including overhead and supervision

At a capacity factor of 0.6, fixed charges amount to 4.7 mills/Kw-hour, operation and maintenance are 0.8 mills/Kw-hour, and power and limestone are also 0.8 mills/Kw-hour.

Representative Japanese FGD costs were given in our previous annual report, and no update has been prepared.

2.2 REGENERABLE FLUE GAS DESULFURIZATION

Process Information

Regenerative FGD processes produce sulfur, sulfuric acid, or other sulfur-containing products which have a potential market value. Currently, such processes are less widely applied than the throwaway processes which were quickly developed during the early days of the Air Quality Act. The throwaway technologies were generally considered less complicated. Regenerable processes currently in use at domestic utilities are magnesium oxide scrubbing and the Wellman-Lord process (which uses Na_2SO_3), both being used only for coal-fired boilers at this time.[33] Japan uses these same processes and others for industrial and utility boilers firing residual oil, as shown in Table 2-5.

The MgO process was selected as the basis for the flow diagram in Figure 2-3, which includes the same venturi-absorber described in Section 2.1. It was selected because it is the only regenerable process to have been applied to a residual oil-fired boiler in the United States.

A slurry of MgO or $Mg(OH)_2$ absorbs sulfur dioxide from flue gas in a scrubber, yielding magnesium sulfite and sulfate. In the scrubbing step, the following reactions predominate:

- SO_2 absorption

$$5H_2O + Mg(OH)_2 + SO_2 \longrightarrow MgSO_3 \cdot 6H_2O\downarrow$$

$$SO_2 + MgSO_3 \cdot 6H_2O \longrightarrow Mg(HSO_3)_2 + 5H_2O$$

- Bisulfite neutralization

$$Mg(HSO_3)_2 + MgO + 11H_2O \longrightarrow 2MgSO_3 \cdot 6H_2O\downarrow$$

- Magnesium sulfite oxidation

$$2MgSO_3 + O_2 \longrightarrow 2MgSO_4$$

TABLE 2-5. REGENERABLE FGD INSTALLATIONS IN JAPAN

Process	Absorbent	By-Product	Total Units[a]	Flue Gas Rate[b]
Wellman-MKK	Na_2SO_3	H_2SO_4 or S	12	5,306,000 Nm^3/h
Wellman-SCEC	Na_2SO_3	H_2SO_4 or S	6	1,289,000 Nm^3/h
Onahama-Tsukishima	MgO	H_2SO_4	1	84,000 Nm^3/h
Chemico-Mitsui	MgO	S	1	500,000 Nm^3/h
Mitsui Mining	MgO	H_2SO_4	1	80,000 Nm^3/h
Mitsui Mining	ZnO	H_2SO_4	1	50,000 Nm^3/h
Shell	CuO	S	1	120,000 Nm^3/h
Sumitomo H.I.	Carbon	H_2SO_4	1	160,000 Nm^3/h
Hitachi, Ltd.	Carbon	H_2SO_4	2	591,000 Nm^3/h
Nippon Kokan	$(NH_4)_2SO_3$	$(NH_4)_2SO_4$	2	1,900,000 Nm^3/h
Kurabo Engineering	$(NH_4)_2SC_4$	$(NH_4)_2SO_4$	1	15,000 Nm^3/h
MHI-IFP	$(NH_4)_2SO_3$	S	1	42,000 Nm^3/h
TEC-IFP	$(NH_4)_2SO_3$	S	1	6,000 Nm^3/h

a. Four units are for utility boilers, sixteen are for industrial boilers, and the rest are for acid plants, Claus furnaces, sintering and smelting plants.

b. 3,000 Nm^3/h corresponds roughly to 1 MW_e.

Source: Jumpei Ando and B. A. Laseke, SO_2 Abatement for Stationary Sources in Japan, EPA-600/7-77-103a, September 1977.

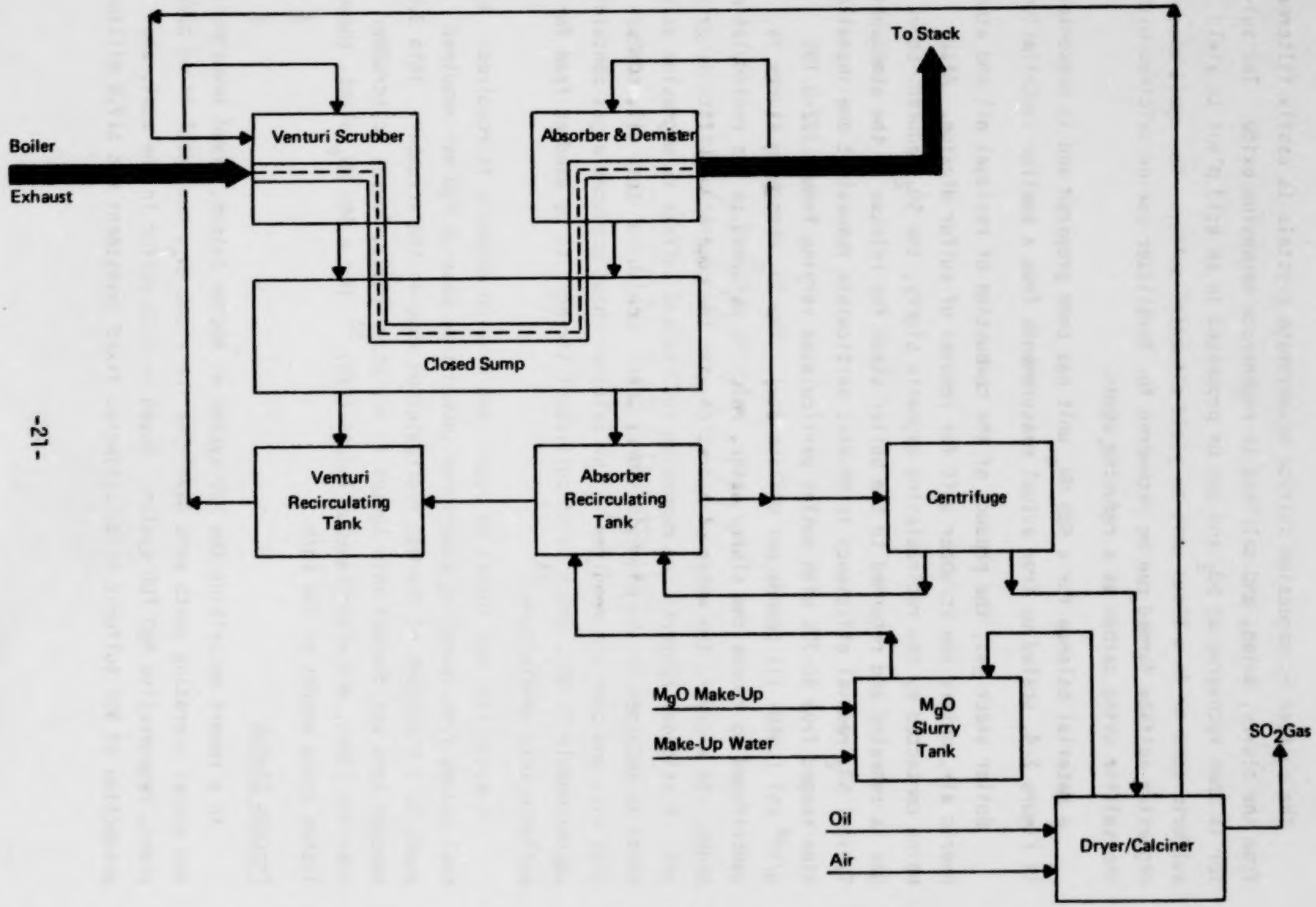

Figure 2-3 - Flow Diagram for a Typical M_gO Process Scrubber

The sulfite as magnesium sulfite hexahydrate crystals is easily filtered from the slurry, dried, and calcined to regenerate magnesium oxide. The sulfur is then recovered as SO_2 and can be processed in an acid plant to yield sulfuric acid or in a Claus unit to yield elemental sulfur. The small amount of magnesium sulfate formed can be recovered for fertilizer use or calcined with the sulfite using carbon as a reducing agent.

A material balance for a 500 MW_e unit has been prepared and is presented in Figure 2-4, scaled up from actual measurements from a smaller installation.

Boiler stack gas, the product of the combustion of residual oil and atmospheric air, enters the scrubber unit for removal of sulfur dioxide. After being contacted by the recirculating magnesia slurry, the SO_2-reduced, stack gas is reheated and returned to the boiler stack for release to the atmosphere. Typical SO_2 removal efficiency is 90-94%; particulate removal at one installation ranged from 46-70% with outlet particulates varying from 0.122-0.199 $g/10^6$ cal (.068-.111 pounds per million Btu). The SO_2 absorbing slurry is centrifuged to remove the slurry water, which is returned to the recirculating tanks. In a dryer, the water of hydration with the magnesium sulfite is driven off. A calciner converts the magnesium sulfite and sulfate to magnesium oxide which is returned to the magnesia slurry tank. Low sulfur fuel oil, combustion air, and coke are required in the calciner which produces a gas containing approximately 7% SO_2, which is of sufficient strength to be used as feed for sulfuric acid manufacture.[24]

In actuality, MgO losses do occur, and make-up magnesia is required. Actual values from operating experience showed that make-up MgO was required equal to 3.5 percent of the MgO recirculation rate in the scrubber. This 3.5 percent loss was divided into losses to the stack (35%), losses to scrubber overflow (38%), and miscellaneous losses (27%).[24] For a 500 MW_e plant, these losses could amount to 150 kg/h.

Process Status

In a report describing the MgO system at Boston Edison, fixed investment and annual operating costs were developed for a 200 MW_e, new, coal-fired power plant, regenerative MgO FGD system. Based on 3.5% sulfur in the coal, and production of 98% sulfuric acid, estimated fixed investment was $17.4 million

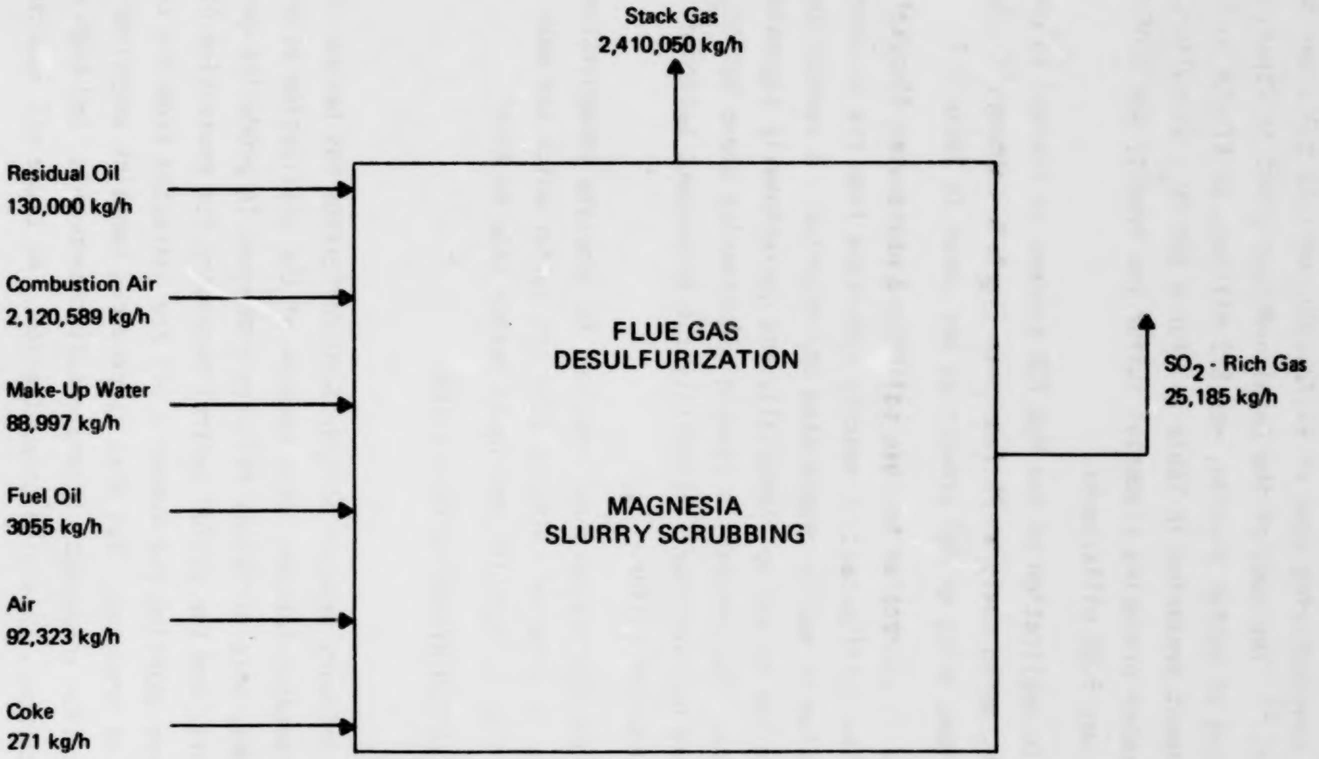

Figure 2-4 - Material Balance for a 500 MWe MgO Process Scrubber

or \$87 per kilowatt (1975 dollars). Total annual costs were \$2,853,045 or 2.04 mills/kw-hr (80% capacity factor).[24] A previous EPA study on a similar basis (1972 dollars) gave a fixed investment of \$11.685 million or \$58.43 per kilowatt, and an annual manufacturing cost of \$1,725,800, or 1.23 mills per kw-hr (80% capacity factor).[27] The cost of the Chemico-Mitsui plant in Japan, exclusive of any processing of sulfur dioxide, was \$13 million, or \$74/KW in 1974. Total capital investment presented in Table 2-3 for a 500 MW_e, 6% sulfur, oil-fired, magnesia scrubber producing elemental sulfur (no credit) was \$106.87/KW, and its annual cost was 5.05 mills/kw-hr.

Current domestic application of the MgO FGD process is limited to one, 120-MW_e installation, using coal, at Philadelphia Electric Company.[33] Japan has three installations using an MgO process as was shown in Table 2-5.

The MgO process is attractive because solids and wastewater disposal problems are avoided. The sulfite salt is readily separated from the scrubber liquor, and the magnesium is easily regenerated and recycled. A centralized regeneration-acid unit can be set up financially and operationally separate from the utility operation. The process is capable of achieving above 90% SO_2 removal efficiency, and has excellent flexibility for by-product switching from sulfuric acid to elemental sulfur.

Drawbacks include the energy input required to generate concentrated SO_2 and the fluctuations in price of sulfuric acid and sulfur which can make the acid plant regeneration a financial detriment rather than an asset.

2.3 HYDRODESULFURIZATION/HYDRODENITRIFICATION

Process Information

The petroleum refinery process of hydrodesulfurization has become viable and necessary in providing residual oils because of the utilization of poorer quality (sour) crudes, more efficient refinery processes in producing gasoline and Number 2 oil, and the sulfur control necessary for protection of the environment. As more gasoline and Number 2 oil are extracted from the crude barrel, less resid is produced. But what is produced contains undesirable components, e.g., sulfur compounds, organo-metallic compounds, and high molecular weight hydrocarbons, in a high concentration. As crude oil reserves are depleted, more sour crudes are used as refinery feedstock, with the increased amounts of sulfur and organo-metallics being concentrated in the resid. Finally, to control sulfur dioxide emissions from utility power generation, without gasification of the oil or post-combustion treatment, a low level of sulfur in the fuel oil is required.

A typical HDS process is shown in Figure 2-5. Residual oil is heated and introduced with hydrogen into the fixed-bed HDS reactor containing the catalyst charge. In the reactor, desulfurization, demetallization, and carbon residue reduction (and, to a lesser extent, denitrogenation and some hydrocracking) occur. The sulfur in the reduced crude combines with the hydrogen to form hydrogen sulfide (H_2S).

$$\text{Organo-sulfur compound} + H_2 \xrightarrow[\text{catalyst}]{} H_2S + \text{LSFO}$$

Most HDS processes utilize fixed-bed reactors with catalysts to lower the optimum operating temperature to reasonable limits. Cobalt molybdenum on an alumina base is a common choice, but a multitude of other catalysts have been and are being used and studied to solve the problems of catalyst life and consistent sulfur removal efficiency.

Bed temperatures typically range from $300^{\circ}C$ to $450^{\circ}C$, and pressures from 2.7 MPa to 21 MPa (400-3000 psig). Hydrogen requirements vary from 500 to 10,000 scf/bbl (84-1680 Nm^3/kl) of oil.[35] A material balance is shown in Figure 2-6. Scaled down from typical operating data, it represents production of low-sulfur fuel oil (LSFO) in the amount required by a 500 MW_e power plant.

The reactor effluent enters a series of flash vessels which separate the stream into liquid, recycle-gas, and sour fuel gas fractions (off-gas). The liquid streams pass to a distillation column for fractionation into low-sulfur fuel oil, middle distillate (or furnace oil), naphtha, and sour fuel gas. The recycle-gas goes to an amine scrubber where the H_2S is removed. It is necessary to remove the H_2S, since its presence in the hydrogen-rich recycle gas would reduce the desulfurization rate. This purified recycle gas is either used as quench gas to moderate the reactor's temperature or mixed with the feed and make-up hydrogen. An amine regenerator (considered as part of the recycle gas treatment) separates the recycle amine and hydrogen sulfide.

The amine regenerator represents a potential pollution source. Spillage, purging, amine disposal, or any other fugitive emissions from the regenerator

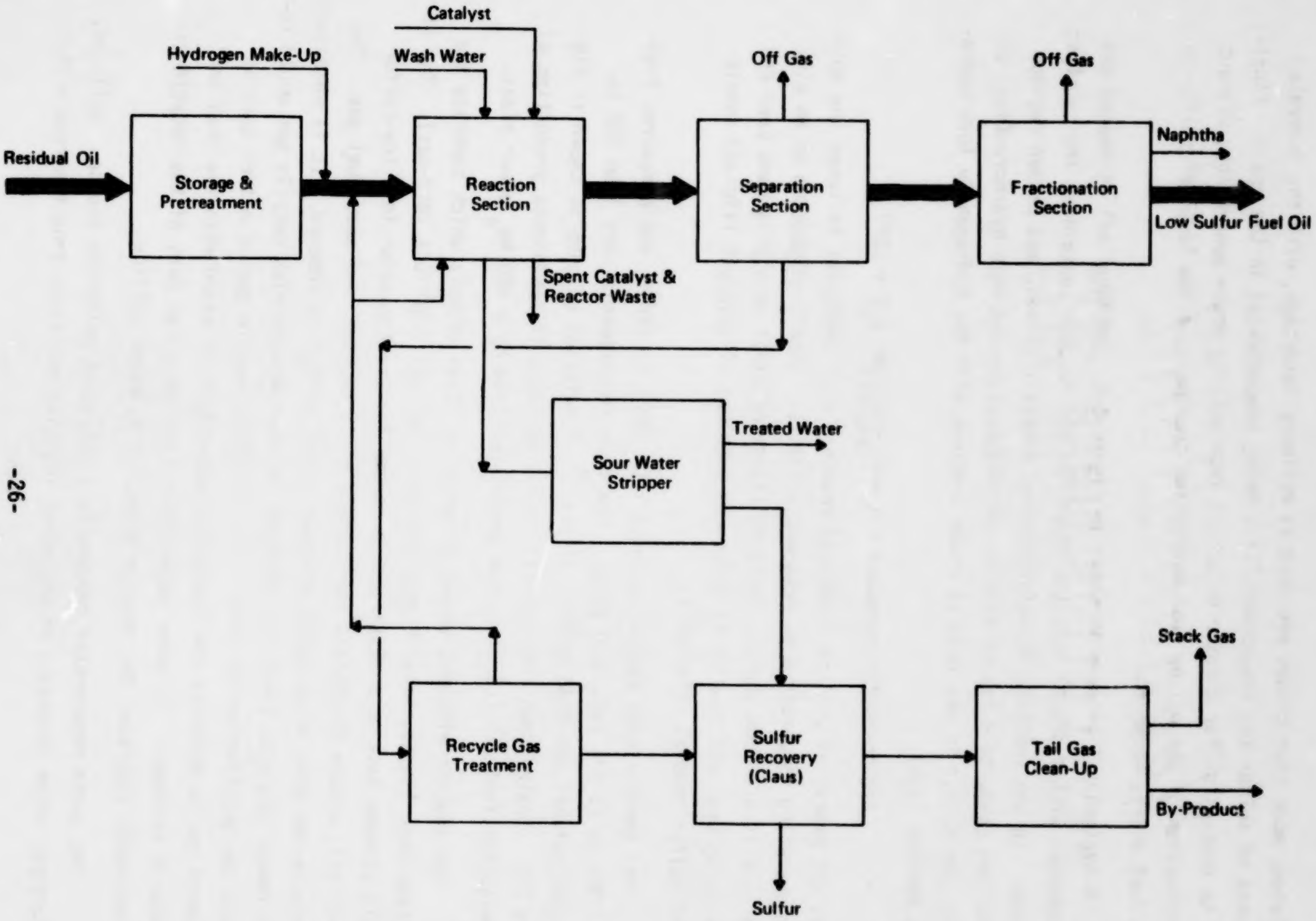

Figure 2-5 - Flow Diagram for a Typical HDS Process

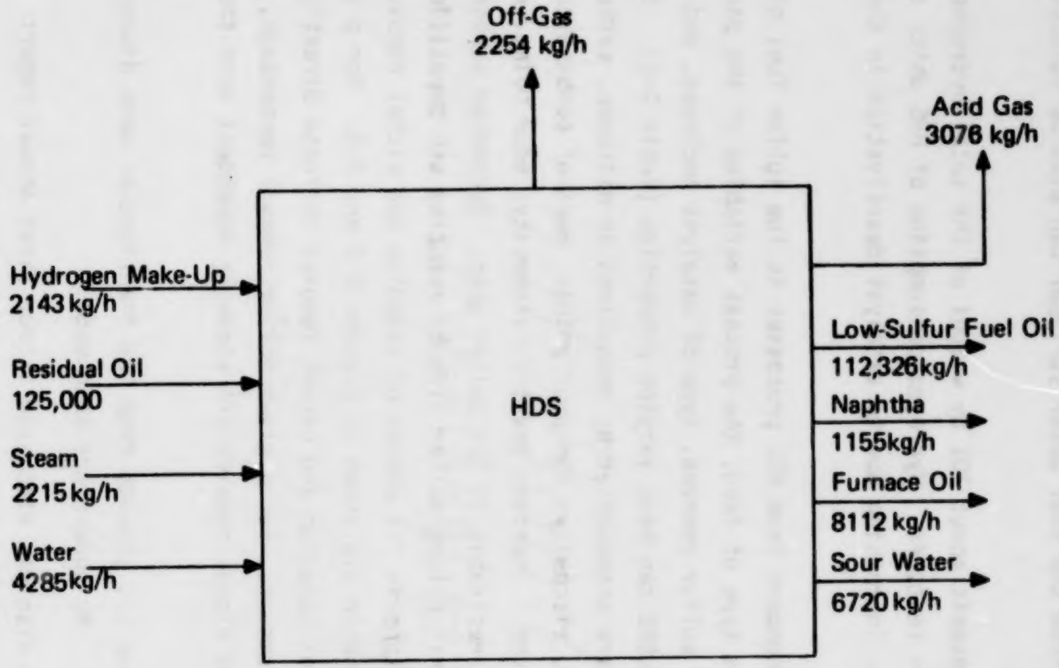

Figure 2-6 - Material Balance for a 500 MWe—HDS Process

present the possibility for a toxic effluent. Work to date has not explored this area in great detail.

The H_2S-rich off-gas stream from the amine regenerator (96-99% H_2S) can be treated in a Claus unit for recovery of elemental sulfur (approximately 97% conversion), with the unconverted H_2S passing from the unit in the form of sulfur dioxide. Additional control, tail-gas cleanup, is required for this SO_2-containing stream. Acid gas from the sour water stripper can also be handled by the Claus unit.

Hydrogen make-up represents about 10% by weight of the total hydrogen and recycle gas utilized in the reactors. Hydrogen consumption of HDS units changes gradually during operation, increasing due to catalyst deactivation in the HDS reactors.

The major product of concern from HDS processes is low sulfur fuel oil (LSFO). Depending upon the type of feed, the process variables of the particular HDS process, the amount of sulfur removed, type of catalyst employed, and number and type of reactors, the LSFO can have varying properties (Table 2-6). Substantial reductions in sulfur are accompanied by reductions in nitrogen, carbon residue, vanadium, nickel, ash, viscosity, and pour point. Heat of combustion and hydrogen content are improved. Improved gravity, viscosity, pour point, and heat of combustion are all desirable to the boiler user. Decreased carbon residue, ash, and metals content prolong boiler life by reducing ash deposition and corrosion. Typical variations in the amount of vanadium and nickel removed as a function of the catalyst chosen are shown in Figures 2-7 and 2-8. For a given catalyst, the percentages of vanadium and nickel removed increase directly with the percentage of sulfur removed. For a given sulfur removal percentage, the percentages of vanadium and nickel removed are strongly dependent upon the catalyst selectivity.[17]

The naphtha and furnace oil streams from the fractionator were discussed in our previous annual report. No update has been made.

The wash water stream also was discussed in our first annual report. Data are still being studied as input to the environmental assessment.

Off-gases produced in the separation and fractionation sections of the HDS process are blended together into a single stream rich in hydrogen and containing

TABLE 2-6. TYPICAL PROPERTIES OF LSFO PRODUCT FROM HDS PROCESSES

	Untreated	1% S LSFO	0.3% S LSFO	0.1% S LSFO
Product Yield: Vol. %	--	89.4	97.5	97.1
Product Properties:				
Cut Point: °F	650	650	375	375
Gravity: °API	16.6	20.0	23.4	24.1
Sulfur: Wt. %	3.8	1.0	0.3	0.1
Carbon Residue: Wt. %	9.0	5.31	3.33	2.75
Nitrogen: Wt. %	0.22	0.13	0.13	0.09
Nickel: PPM	15.0	4.6	1.3	0.4
Vanadium: PPM	45.0	8.2	2.2	1.0
Viscosity: SUV (210°F)	250	107.3	52	45
Ash: Wt. %	0.02	0.004	0.003	0.003
Salt: PPM *	44.9	0	0	0
Heat of Combustion: Btu/Lb		19,110	19,250	19,375
Hydrogen: Wt. %		12.1	12.5	12.7
Carbon: Wt. %		86.7	87.1	87.1
Pour Point: °F		+60	+35	0
Hydrogen Consumption: SCF/BBL		497	663	812

* Salt refers to all water-soluble cations, determined as halide and reported as NaCl before desalting.

Source: Gulf Research and Development Company

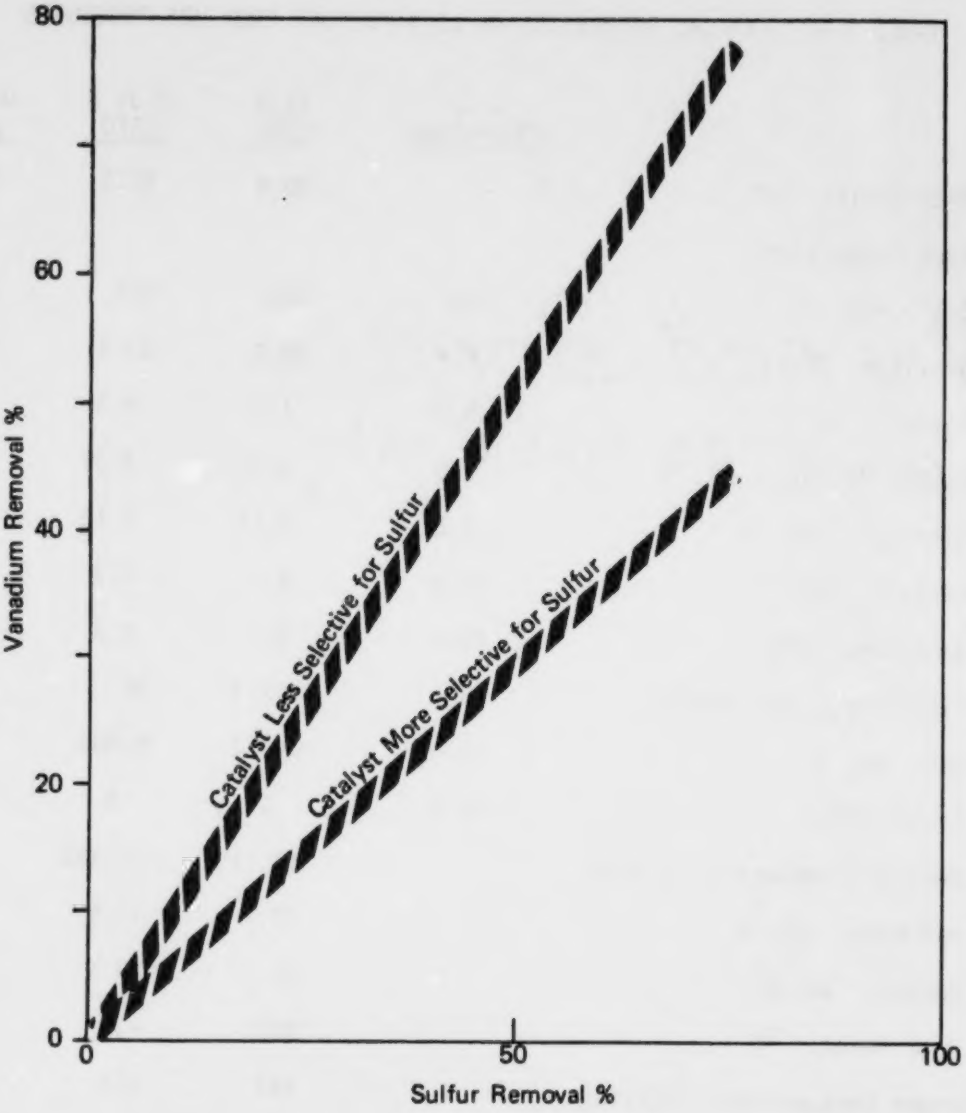

Figure 2-7 - Catalyst Effect on LSFO Properties
Vanadium Removal

Source: Hastings, Kenneth E., Lewis C. James, and William R. Mounce, "Demetallization Cuts Desulfurization Costs," The Oil and Gas Journal, LXXIII, No. 26 (June 10, 1975) pp. 122-130.

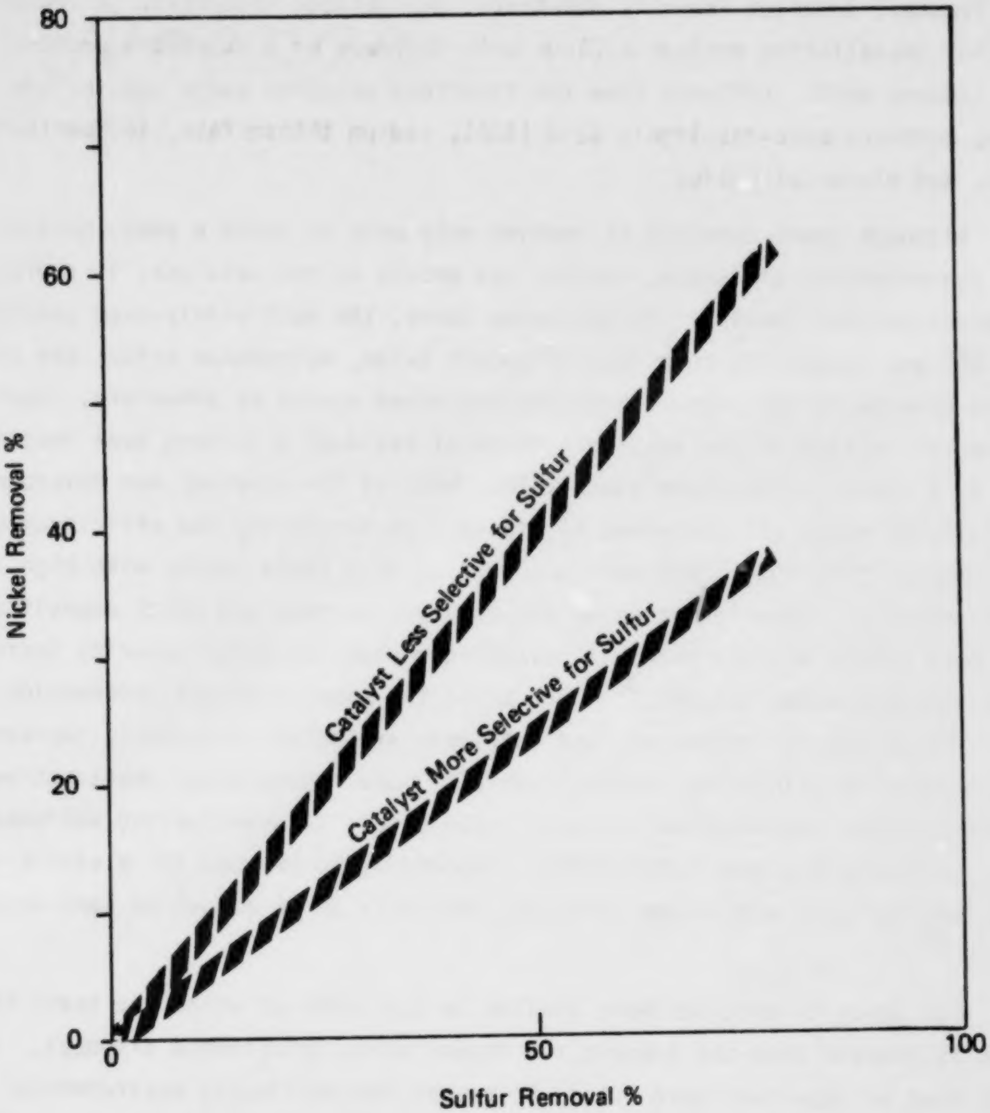

**Figure 2-8 - Catalyst Effect on LSFO Properties
Nickel Removal**

Source: Hastings, Kenneth E., Lewis C. James, and William R. Mounce, "Demetallization Cuts Desulfurization Costs," The Oil and Gas Journal, LXXIII, No. 26 (June 10, 1975) pp. 122-130.

about 15 mole percent hydrogen sulfide. Its eventual end use is determined by the particular refinery complex, but it is not emitted to the atmosphere.

Acid gas treatment was described in our previous annual report, and a variety of tail gas treatment methods was reviewed, including the Shell Claus Off-Gas Treater, Institut Francais dePetrole, and Chiyoda Processes. A recent commercial installation employs a Claus unit followed by a Stretford process tail gas cleanup unit. Effluent from the Stretford solution purge can include vanadium, anthraquinone-desulfonic acid (ADA), sodium thiosulfate, sodium thiocyanate, and elemental sulfur.

Although spent catalyst is removed only once or twice a year, because of the concentration of carbon, sulfur, and metals on the catalyst, it represents an environmental concern. As mentioned above, the most widely-used catalysts for HDS are composites comprised of cobalt oxide, molybdenum oxide, and alumina, where alumina is the support carrying the other agents as promoters. Over 250 processes related to the desulfurization of residual oils have been described in the U. S. patent literature since 1970. Most of the research and development activity by major oil companies has focused on increasing the efficiency of sulfur removal from total feed systems, particularly those resids with high asphaltene contents. Coke formation on the catalyst surface and metal deposition at the pore mouths are the catalyst poisoning mechanisms whose severity increases with the asphaltene content.[32] Such being the case, catalyst information is restricted by the oil companies, and catalysts are being continually improved. Metal deposits within the catalyst can also make regeneration unattractive, especially since regeneration converts these metals to deactivating sulfates. Many catalysts are made sufficiently inexpensive to be used for a single cycle and then replaced with a new catalyst, generally on an annual or semi-annual basis.[15]

Our study to date has been limited to the point at which the spent catalyst is removed from the process for regeneration or ultimate disposal. It is felt that an important need exists to assess the multimedia environmental impact of spent hydrodesulfurization catalysts by regeneration and final disposal and to provide a total view of the fate of important potential pollutants which may be reprocessed or disposed of with spent catalysts from the hydrodesulfurization processes.

Process Status

The major current commercial, direct hydrodesulfurization facilities were described in our previous annual report. To that list can be added Exxon's Baytown Residfiner 1 with a 75,000 barrel-per-day capacity.

Present estimates for the desulfurization of reduced crude range from \$2 to \$4 per barrel. The cost depends on items such as hydrogen cost, site of plant, raw material costs, and desired amount of sulfur in end product.

In a refinery complex, many of the process units (for example, sour water strippers, acid gas cleanup) are not dedicated to HDS alone, and the apportionment of costs is difficult to ascertain.

Data obtained on Japanese units are being analyzed, with the ultimate objective of determining the range of desulfurization for the actual operating units. Total capital costs were obtained for all seven plants visited, but problems were encountered in establishing an equal basis for comparison. In some cases, the cost included sulfur recovery and tail gas treatment, while in others, this cost was left out. Economic information on the Baytown unit is just becoming available.

No update on energy efficiency or process applicability was prepared during this contract year.

Hydrodenitrogenation

Although hydrodenitrogenation (HDN) is of greater importance in lowering the organo-nitrogen content of synthetic crudes extracted from oil shale, some coals, and certain low-grade naturally-occurring petroleums, HDS reactions occur in the HDS process and improve the quality of the low sulfur fuel oil produced (Table 2-6).

The reactions are similar to those for HDS:

$$\text{Organo-nitrogen compound} + H_2 \xrightarrow[\text{catalyst}]{} NH_3 + \text{LSFO}$$

The HDS and HDN reactions can and do interact with each other, sometimes being mutually inhibiting, sometimes enhancing each other.

Decreased nitrogen is advantageous in that some of the nitrogen oxide emissions from combustion are reduced. Combustion modification and other techniques can usually be used to control total NO_x within current environmental restrictions.

2.4 PARTIAL OXIDATION

Process Information

POX or Partial Oxidation processes convert hydrocarbons into a fuel gas by controlled partial oxidation with air or oxygen. No catalyst is required, thus a wide range of unusable fuels can be converted to clean gaseous fuels. Substantial variations in the sulfur, nitrogen, and metals content of the feedstock are possible.

A flow diagram for a typical POX process is given in Figure 2-9. An accompanying material balance for a POX process producing enough low-Btu gas for 500 MW_e is given in Figure 2-10.

Residual oil is often contaminated by salt water during transportation. To prevent damage to the reactor's ceramic lining, the salt content in the oil feed should be reduced to 10 pounds per 1,000 barrels or less (approximately 30 ppm NaCl or 10 ppm Na). In the fuel preparation section, water washing, followed by electrostatic precipitation or centrifuging to remove the salt water, is usually adequate. Filtration and heating are included as part of the feed preparation.

In producing a low-Btu gas (approximately 5000 kJ/Nm^3 or 125 Btu/scf) for use in a boiler, gas turbine, or combined cycle power plant, air is used as the oxidant. (The use of pure oxygen results in a higher-Btu gas of approximately 12,000 kJ/Nm^3 or 300 Btu/scf, and steam is required as a moderator or dilutant in the reaction.) Pressurized air and residual feed are intimately mixed in the POX reactor producing a fuel gas which contains carbon monoxide and hydrogen. The sulfur in the fuel is converted to hydrogen sulfide in the gasifier's reducing atmosphere. Much of the metallic ash is sequestered with the free carbon or soot, which is removed from the product gas in the carbon/gas separator section. The balance of the ash is deposited in the reactor and removed during periods when the reactor is shut down for inspection.[35]

A waste heat exchanger at the outlet of the reactor recovers much of the reactor heat in the form of steam, adding greatly to the overall process efficiency. Additional heat recovery may be obtained from the product gas after slurry separation and before gas scrubbing in the carbon/gas separator section.

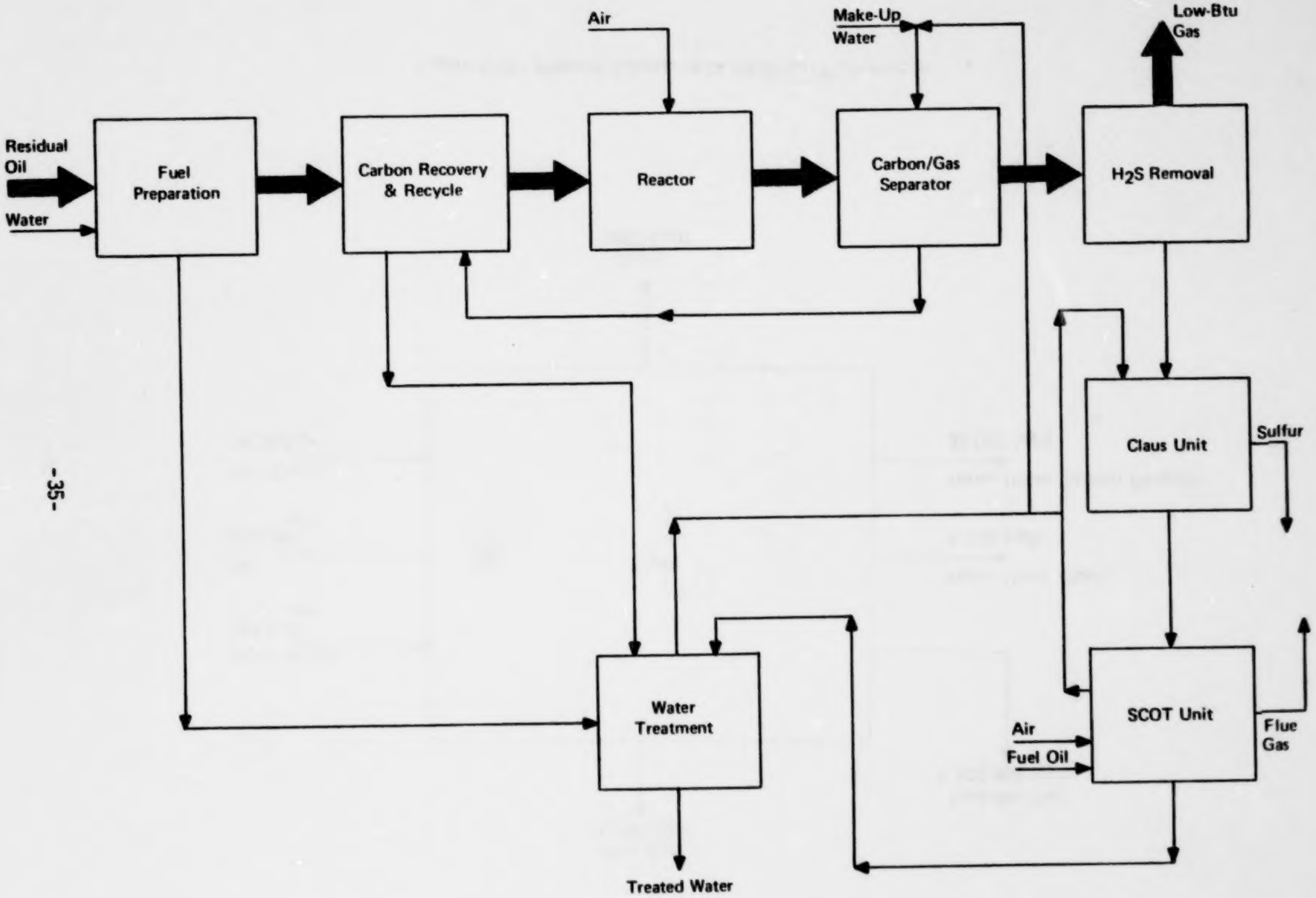

Figure 2-9 - Flow Diagram for a Typical POX Process

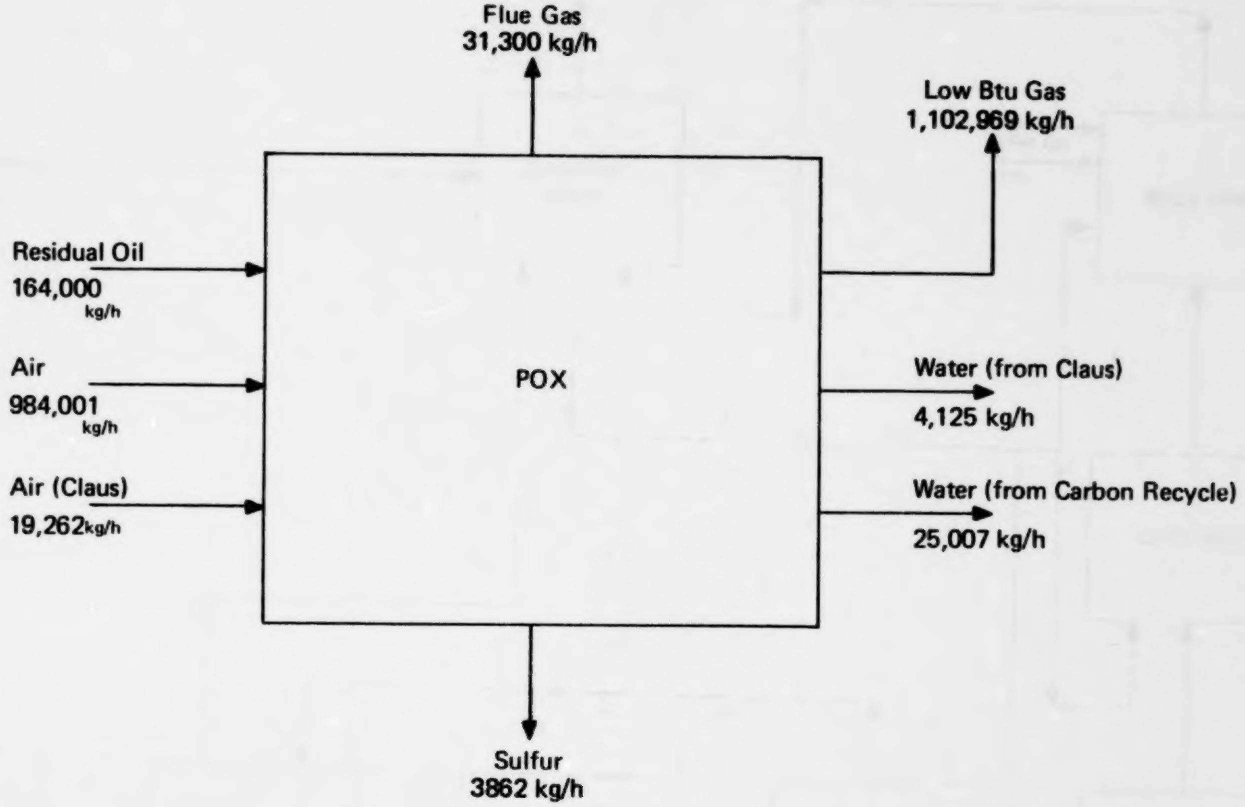

Figure 2-10 - Material Balance for a 500MWe - POX Process

In the carbon/gas separator section, the product gas from the reactor is contacted by water in a spray vessel followed by a carbon slurry separator; most of the soot is recovered here. The remaining soot is removed from the product gas in a scrubber. The water wash is designed to remove essentially all of the product gas contaminants that are soluble in water, plus the carbon soot and certain ash compounds which remain suspended in the water. These contaminants are mainly carbon, ash, including vanadium and nickel compounds, hydrogen cyanide, ammonia, and traces of formic acid. All of these contaminants are potential pollutants and should be handled accordingly. By treating the spent wash water, either directly or after returning the soot to the carbon recovery and recycle section, the hydrogen cyanide, formic acid, and ammonia can be disposed of safely, leaving only the metals and ash.

Two major methods are used in the carbon recovery and recycle section where soot is separated from the water slurry. A pelletizing system recovers and agglomerates the soot to carbon pellets with the aid of either a distillate or residual oil. The water is returned to the carbon/gas separator section, while the soot pellets can be burned in specially-developed pellet combustors or returned to the reactor feed. The other separation method utilizes an intermediate fluid, naphtha, to preferentially wet the carbon, producing a naphtha-soot agglomerate which can then be separated from the water stream. The naphtha-carbon agglomerates are then mixed with fresh oil feed (which can be the residual feed) and flashed into a naphtha stripper for recovery of the naphtha. The carbon-fuel oil combination is then recycled to the reactor for conversion into product gas. Some ash, vanadium, and nickel are still retained by the soot, and thus recycled back through the process for eventual disposal either with the wash water or the reactor ash.[38]

The sulfur products are only slightly soluble in water and therefore remain in the product gas stream as hydrogen sulfide (H_2S), with some carbonyl sulfide (COS) and a trace of carbon disulfide (CS_2).

Several commercial processes are available for removal of up to 99+ percent of the H_2S from the product gas. Some absorption processes use solvents which selectively remove the H_2S, leaving much of the CO_2 in the gas. The carbon dioxide can be absorbed if another solvent is chosen, yielding a product gas with a higher Btu content; but, it is usually retained in the product gas, especially if the product gas is to be used as a fuel for gas turbines where it has some beneficial effect. High temperature processes which do not require any cooling of the product gas stream are available; but, few, if any, have achieved commercial status. The product gas, cleaned of most of the soot, sulfur, ash, and particulate, exits the H_2S removal section and is suitable for use as a gas turbine, steam boiler, or combined-cycle fuel. A typical analysis of this low-Btu product gas is given in Table 2-7.

The hydrogen sulfide can be converted into elemental sulfur, leaving an effluent gas containing some residual sulfur dioxide, a potential pollutant. However, further processing methods, which will reduce the sulfur dioxide emission to very low levels, are available.

The water streams can be collected and processed in the water treatment section. Included in these water streams are soluble and suspended ash components, including vanadium and nickel, minor quantities of carbon, hydrogen cyanide, and ammonia, and trace amounts of formic acid.

Process Status

No update of the POX process status has been prepared for this annual report. Except for inflation, capital and operating costs previously described remain unchanged. No POX installations or new gasifier installations have become known.

Intensive private and governmental development work in the areas of hot gas cleaning for the product gas and increased gas turbine operating temperatures will enhance the future potential of the POX process when integrated with a combined-cycle power generation unit. The combined-cycle concept is expected to assume a major role in the production of electricity in the near future. The POX process and the combined-cycle concept complement each other. The POX gasifier produces clean fuel required by the high temperature gas turbine, and the gas turbine produces large quantities of compressed air required by the POX process. Sensible heat carried by the fuel after gasification may be used to produce steam for the steam turbine. The high quantity of inert gas in the low-Btu product also reduces NO_x emissions from the gas turbine. The overall thermal efficiency of a gasification/combined-cycle system has been estimated at 38 to 40 percent.[18, 36, 39]

TABLE 2-7. TYPICAL LOW-BTU GAS COMPOSITION FROM PARTIAL OXIDATION

Composition	Volume %
Hydrogen	14.3
Carbon Monoxide	23.7
Carbon Dioxide	0.02
Water	0.28
Methane	0.26
Nitrogen	60.65
Argon	0.76
Hydrogen Sulfide	< 300ppm
Carbonyl Sulfide	
Total	100.00
Average Molecular Weight	24.33
Higher Heating Value, kJ/Nm^3	4965 (125.5 Btu/SCF)
Lower Heating Value kJ/Nm^3	4668 (118.0 Btu/SCF)

Source: Catalytic, Inc., "Process Technology Background for Environmental Assessment/System Analysis Utilizing Fuel Oil," 68-02-2155, EPA-600/7-77-081, August, 1977.

2.5 CHEMICALLY ACTIVE FLUID BED

Process Information

Fluidized-bed combustion includes both atmospheric and pressurized processes. Possible variations include steam tubes in the fluidized bed, air tubes, or no tubes, whereby a hot, low-Btu gas is produced for subsequent generation of electric power. The burning (or gasification) of oil or coal occurs within a bed of granular, noncombustible material such as limestone. This bed is supported on a grid, and air is passed up through the plate, causing the granular material to become suspended (fluidized).

Process advantages for gasification include:

- in situ removal of SO_2 by the use of limestone as a bed material;
- more fuel flexibility than a conventional boiler, which can result in reduced fuel costs from the use of cheaper fuels; and
- production of a gaseous fuel usable, with little equipment modification, in existing oil- and gas-fired boilers which may be legislatively banned from using low-sulfur fuel oil or natural gas.

Additional advantages when fluidized-bed combustion is used in place of a conventional boiler are:

- reduced boiler size and heat transfer surface requirements, thus, the possibility of modular instead of the more expensive field construction; and
- reduced NO_x emissions, trace element volatilization, and corrosion due to lower combustion temperature (about 900^oC vs. 1500^oC for a conventional boiler).

The Chemically Active Fluidized-Bed (CAFB) is an atmospheric-pressure, fluidized-bed, residual oil gasification/desulfurization process. Figure 2-11 is a flow diagram for a typical CAFB installation. The basic CAFB process consists of four distinct functions: oil gasification/desulfurization, lime regeneration, sulfur recovery, and spent stone disposal/processing. High-sulfur fuel oil is injected into an 870^oC bed of limestone fluidized by a mixture

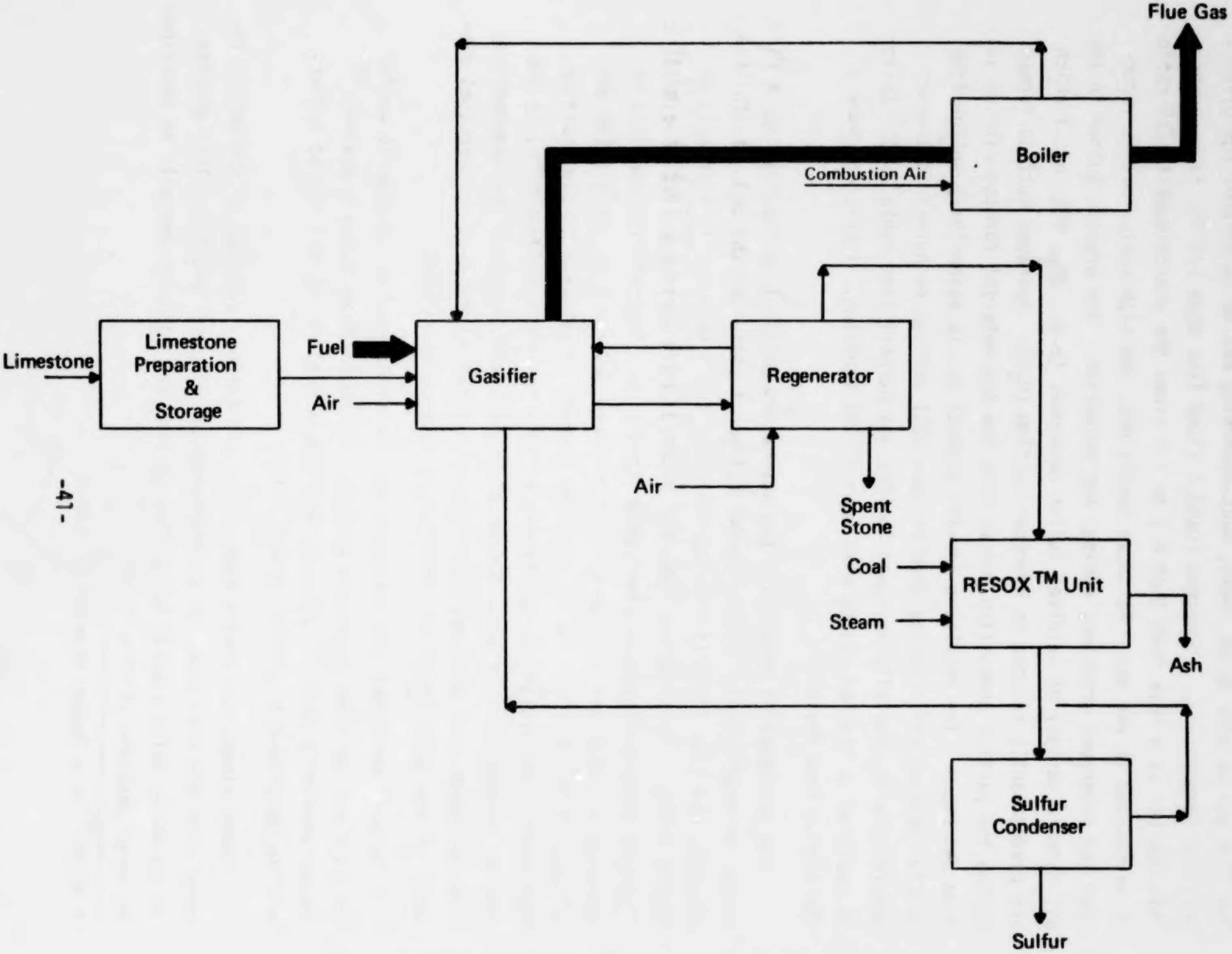

Figure 2-11 - Flow Diagram for a Typical CAFB Process

of flue gas and air. Air is admitted in sub-stoichiometric proportions (approximately 22 percent) to limit the amount of oil combustion and heat release. The flue gas is used as an inert, heat-absorbing medium to control the overall gasifier temperature. Limestone ($CaCO_3$) sized less than 1/8 in. is injected into the bed at a rate such that 0.5 to 1.5 times the stoichiometric CaS ratio is maintained in the bed. At these conditions, the high-sulfur oil is vaporized and undergoes cracking, coking, and oxidation. The organic sulfur in the oil forms a variety of oxidized sulfur compounds (e.g., SO_2, COS, etc.) which are predominantly reduced to hydrogen sulfide (H_2S). Hydrogen sulfide formed during the partial combustion reacts with the bed material forming calcium sulfide and steam. The resulting low-Btu product gas is essentially sulfur free (sulfur removal efficiencies greater than 90%) and can be burned in a steam generator with specially-designed low-Btu gas burners (see Table 2-8). Sulfur is captured in the bed, along with most of the vanadium, nickel, and some of the sodium from the oil.

The bed material containing the sulfur and metals from the oil can be discarded or regenerated. As the concentration of sulfur on the bed material increases, the lime (from in-situ calcining of the limestone) is less able to absorb sulfur. This sulfur-laden bed material must be removed from the gasification zone and replaced with sulfur-free lime. Regeneration consists of reacting air with the calcium sulfide to yield CaO and a sulfur dioxide gas of about 8 to 10% SO_2. The regenerated sorbent is returned to the gasifier. Regenerator temperature is maintained at 1050 to 1100°C (1922-2012°F) by the rate of sorbent circulation. Sulfur absorption efficiency of the regenerated lime decreases with each regeneration, necessitating the need for eventual disposal of the spent stone and addition of make-up limestone.

Several processes are available for converting sulfur dioxide to sulfur (e.g., Claus tail gas catalytic process, Bureau of Mines citrate system).[22] Foster Wheeler's RESOX^{TM*} process, which uses coal to convert SO_2 to sulfur, will be described in greater detail later.

Spent stone, containing some sulfur and carbon, and most of the metals removed from the oil, presents an environmental disposal problem. This problem is currently being studied by various persons and agencies and will be described in other sections of this report.

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* RESOX^{TM} is a Foster Wheeler trademark.

TABLE 2-8. TYPICAL CAFB PRODUCT GAS COMPOSITION

Component	Volume Percent
Hydrogen	8.6 ± 3.0
Nitrogen	61 ± 5
Methane	6.4 ± 1.0
Carbon Monoxide	10 ± 3
Carbon Dioxide	9.5 ± 2.0
Ethylene	4.3 ± 0.6
Ethane	0.12 ± 0.04

Higher Heating Value 7700 kJ/Nm^3 (195 Btu/SCF)

Source: Craig, J. W. T., et al., "Chemically Active Fluid-Bed Process for Sulphur Removal During Gasification of Heavy Fuel Oil - Third Phase," EPA-600/2-76-248, September 1976.

The specific installation selected for detailed study is the 17-MW_e CAFB demonstration plant at Central Power and Light Company (Corpus Christi), La Palma station in San Benito, Texas. Design flow rates for this installation are the basis for the 500 MW_e material balance shown on Figure 2-12.[43] Process development originated with the gasifier pilot-plant work at Esso Research Center Abingdon (ERCA), United Kingdom, in 1966.[13] The U. S. EPA has contracted with Foster Wheeler Energy Corporation (FWEC) the design of the demonstration plant. FWEC has, in turn, signed a separate contract with Central Power and Light so that EPA is sponsoring the design and testing and CPL is sponsoring the construction and operation.[34]

The CAFB gasifier/regenerator is a single unit which performs the two functions of gasification and sorbent regeneration. Transfer of bed material from the gasifier to the regenerator and return is accomplished in bed material transfer conduits by the pulsation of high-pressure flue gas admitted to the conduits. The recirculation rate is determined largely by the sulfide formation rate in the bed but is affected by the need to circulate bed material through the regenerator to absorb excess heat and limit the overall regenerator temperature. Bed material for the CAFB, as for most fluid bed combustion designs which remove sulfur, is limestone.

The limestone to be used in the CAFB demonstration unit is that shown in Table 2-9.

The RESOX unit mentioned above is a development of FWEC. Regenerator off-gas, consisting of sulfur dioxide, carbon dioxide, and nitrogen, passes through a cyclone before entering the RESOX reactor at a temperature of 650°C (1200°F). (Fines are discarded with the spent stone from the regenerator.) This temperature is maintained by cooling the off-gas with injected steam which also produces the required H_2O/SO_2 ratio. Control air is also added to the RESOX inlet to furnish oxygen to maintain and control the reactor temperature at 760-816°C (1400-1500°F). The reduction reaction

$$SO_2 + C \longrightarrow CO_2 + S$$

is exothermic but cannot maintain the temperature necessary for the high conversion of SO_2 to sulfur. Carbon is added to the RESOX reactor in the form of anthracite coal.

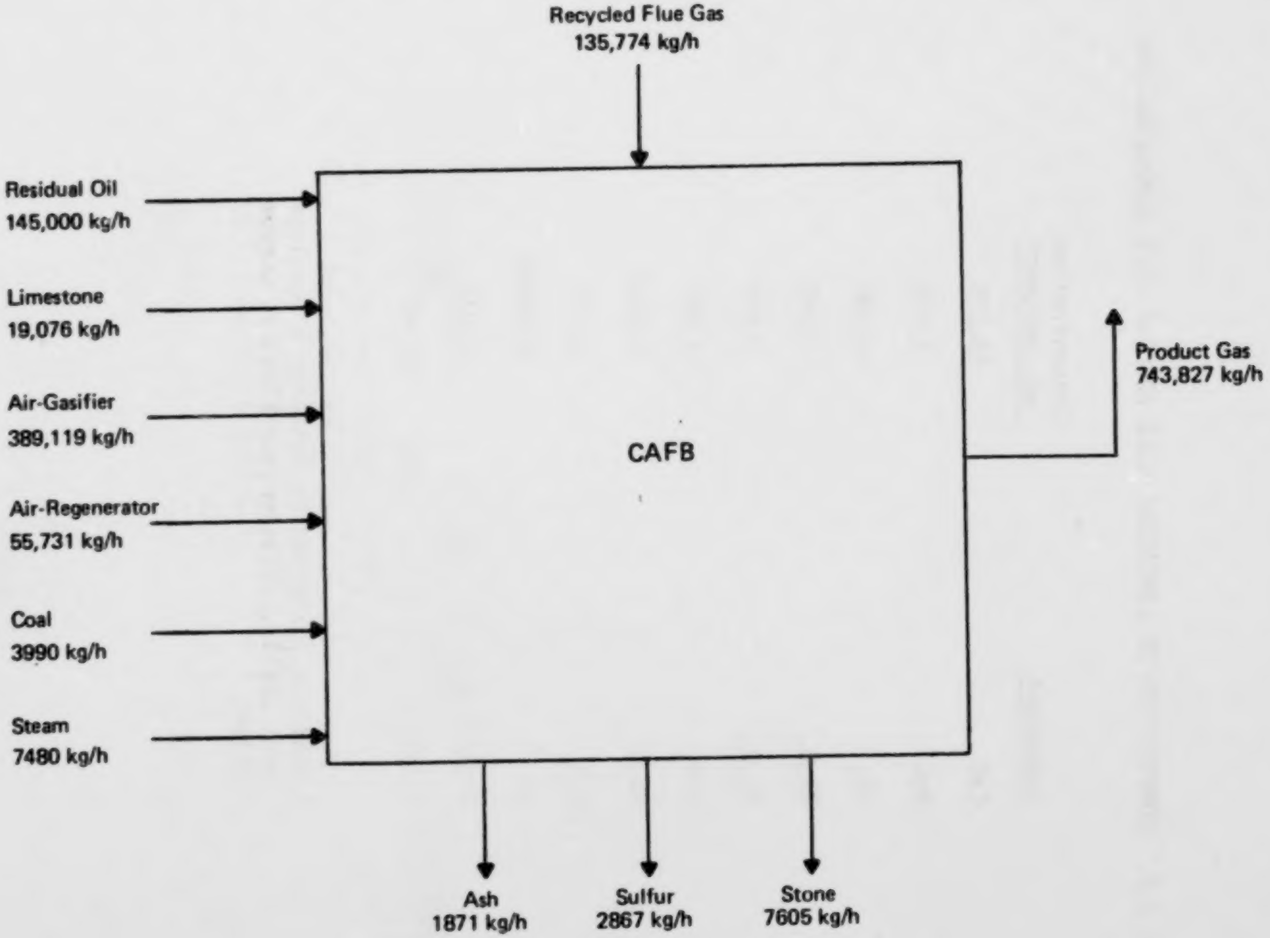

Figure 2-12 - Material Balance for a 500 MWe CAFB Process

TABLE 2-9. COMPOSITION OF LIMESTONE USED FOR THE CAFB DEMONSTRATION

Component	Concentration, wt. percent*
CaO	53.27%
MgO	0.53%
CO_2	43.58%
Al_2O_3	0.94%
Fe_2O_3	0.97%
SiO_2	1.84%
Na_2O	0.026%
K_2O	0.17%
Cl	0.0032%
Organic C	0.07%
Total	101.4%

* Analysis performed by Research & Development Center, Westinghouse Electric Corporation.

75 to 90% of the sulfur dioxide entering the reactor exits as elemental sulfur after being cooled in a sulfur condensing heat exchanger. The unreacted SO_2 is returned to the gasifier.

The major discharge stream and the major reason for existence of the CAFB is the boiler flue gas. Low-Btu gas output from the CAFB unit, after passing through a cyclone, enters the low-Btu burners in the existing plant boiler. Fines are returned from the cyclone to the gasifier. Compared to conventional combustion, when burning gasified residual oil, sulfur dioxides in the flue gas are eliminated, nitrogen oxides are greatly reduced, and particulates are controllable.

FWEC air emissions calculated and predicted are given in Table 2-10. NO_x emissions are expected to be below the EPA standard for oil and similar to the standards for natural gas primarily because of the low adiabatic flame temperature for low-Btu gas and the dilution effect of the great volume of inert gas in the low-Btu product gas. Sulfur dioxide, of course, is controlled by the removal of sulfur in the gasifier. Particulate emissions are difficult to calculate for the CAFB because of the many variables to be considered, e.g., cyclone efficiency, ash content of the feedstock, carbon content of the particulate, and velocity through the bed.[28] Test results from ERCA have a wide range above and below the EPA standard for No. 6 oil burning.[42] Verification of CAFB particulate emissions must await demonstration unit testing.

Spent bed material from the regenerator will consist primarily of CaO with small amounts of calcium sulfide and calcium sulfate. The expected output rate of 0.08 Kg/s or 610 lb/hr for the demonstration plant is approximately 7605 kg/hr (16,769 lb/hr) for a scaled 500 MW_e plant. Possibly, this material could be sold in its effluent form, or even processed to be made commercially acceptable. If no market exists for this material, it must be processed (e.g., by dead burning) prior to disposal, since CaO and CaS react exothermically with water. Methods of processing and disposal are currently being investigated.

The RESOX unit produces a solid waste of approximately 75 percent carbon and 25 percent ash with small amounts of sulfur. This material has a heating value of approximately 24.4 MJ/Kg (10,500 Btu/lb) and is acceptable for use as a low-sulfur fuel.

TABLE 2-10. ESTIMATED COMPARISON OF EMISSIONS FROM CAFB

	Emissions - lb/10^6 Btu (mg/MJ)					
	NO_x		SO_2		Particulates	
Steam Generator Fuel	Est.	EPA Std.	Est.	EPA Std.	Est.	EPA Std.
Natural Gas	0.18 (77)	0.2 (85)	--	--	--	--
No. 6 Oil	0.45 (192)	0.3 (128)	2.9 (1,240)	0.8 (342)	0.076 (33)	0.1 (43)
Coal	0.72 (307)	0.7 (299)	6.97 (2,982)	1.2 (513)	10.7 (4,577)	0.1 (43)
Low-Btu Gas From No. 6 Oil	0.18 (77)	--	0.76 (325)	--	0.1 (43)	--
Low-Btu Gas From Coal	0.18 (77)	--	1.09 (466)	--	0.1 (43)	--

Source: McMillan, R. E. and F. D. Zoldak, "A Discussion of the Chemically Active Fluid Bed Process (CAFB)," Frontiers of Power Technology Conference, October 26 and 27, 1977.

Process Status

Current cost figures for the CAFB demonstration unit are somewhat meaningless if one is attempting to compare it directly with the other processes discussed in this report. It is a retrofit, demonstration unit, and the published costs do not reflect initial engineering required for system design and equipment specification. Published costs for this unit are in FWEC's preliminary process design manual.[43] Some preliminary capital and operating costs were developed in 1975. Values ranged from $102/kW to $190/kW and from 3.28 mills/kW-h to 6.25 mills/kW-h, dependent upon unit size and other variables.[21] Although these numbers are out of date and were generated before the CAFB demonstration design and construction were begun, they are of the same order of magnitude as the costs for other processes considered in this report.

FWEC has produced a performance comparison for the CAFB demonstration unit; calculated boiler efficiency for the La Palma unit fired with natural gas was 84.53% as opposed to 84.03% for a cold CAFB gas. Overall plant efficiency was 23% using natural gas and 21% burning and producing the CAFB gas. Overall plant efficiencies are low due to the 30-year age of the La Palma unit. On a newer unit, overall efficiencies were calculated as 34% on natural gas and 30% on CAFB gas.

The CAFB shares the wide fuel flexibility of the fluidized bed type of combustion. FBC units are now being operated and developed for most classes of coal. The CAFB pilot plant at ERCA is now being tested on samples of Texas lignite, which will also be gasified later in the CPL demonstration plant. The CAFB for power generation from electric utilities is expected to have none of the feedstock restrictions which other processes such as HDS and POX require.

2.6 SUMMARY

Section 2 has presented updated information on Phase I processes, those which are operating or in commercial design. The CAFB, a Phase II demonstration plant design, has been introduced into the discussion. No attempt has been made to closely compare each process on the basis of economics or environmental impact. Such a comparative evaluation has not been planned for this past year's work, but it will be a part of this project's final report. A summary, by process, of some of the major environmental problems and areas for further engineering study follows.

Japanese units form the basis for the information on non-regenerable FGD processes. All U. S. units operate on coal-fired boiler stack gas. The non-regenerable FGD process has solved an air pollution problem but has created a solids disposal problem. Although the Japanese are able, in some cases, to use the gypsum output from the lime/limestone scrubbers as a marketable by-product, in the U. S. it becomes a throwaway sludge which requires a large amount of land space when dumped into a settling pond. Lined ponds merely contain the sludge, and leaching of pollutants in unlined ponds continues to be an environmental problem. The water required can represent use of a scarce resource in some areas of the U. S. Operating availability of the FGD unit is still a problem, and the entire installation is an added cost in capital and operation for the utility.

Regenerable FGD systems, although requiring more energy (for by-product processing) than non-regenerable FGD systems, offer the potential for lower overall costs by producing a usable and marketable by-product. This potential is somewhat elusive due to the changing needs of the by-product sulfur market and the capital investment required to build a separate processing plant (e.g., a sulfuric acid plant) for by-product reclamation. Such a plant would experience a variable feed composition and flow as the FGD and utility operation varied with power demand and unit availability.

Fugitive emissions present a potential environmental problem when fine particle sorbents such as MgO are used. All regenerable FGD systems for residual oil are in Japan. Even there, the regenerable FGD process systems are not as well established as the non-regenerable FGD systems are for utility boilers.

Although designed for SO_2 removal, both types of FGD processes do well in removing particulates (40-80%) and NO_x (50-90%). Nitrogen oxide scrubbers, which may be incorporated into FGD units, are currently being developed in Japan. The environmental hazard , if any, associated with the particulates not removed, is an area for further study.

HDS processes remove most of the sulfur and heavy metals from the residual oil. However, the sulfur and heavy metal concentrations on HDS catalysts are major points of concern. Spent catalyst regeneration and disposal are problems still to be evaluated. The high initial investment and the cost of hydrogen affect the economics of HDS vis-a-vis the other processes described here. HDS units are built on a refinery scale, supplying more oil product than most individual utility stations require. The development of environmental goals is difficult because of interconnection of the HDS process with many other refinery ery streams, and because of the number and complexity of waste streams and treatment schemes. Operating experience to date has been largely with light Arabian reduced crude, a relatively easy feedstock to desulfurize.

The POX process is very well developed, especially the gasification phase. No combined-cycle POX installations exist, however. For electric power generation, because of the low-Btu output, the POX gasifier must be coupled with a boiler or, preferably, a gas turbine combined-cycle. Its utilization depends upon the acceptance of the combined-cycle concept and the development of high efficiency cycles. Final disposal of the carbon soot by-product and/or reactor ash and the wash water are major environmental concerns.

The CAFB process appears to be outstanding as a retrofit gasifier to existing natural gas or oil-fired boilers. For economic reasons, the low-Btu gas must be used on-site. Fugitive emissions are controlled by designing the bed material regenerator within the same housing as the gasifier. Spent stone disposal will require further study. Particulate control in the product gas, which contains bed material, is a problem to be solved. Based on test results from the demonstration unit, economic and performance data need further attention.

SECTION 3

CURRENT ENVIRONMENTAL BACKGROUND/OBJECTIVES DEVELOPMENT

Environmental assessment involves the determination of contaminant levels associated with emissions and effluents from a point source, and the comparison of those determinations with desirable control levels.

A knowledge of the existing decisions, limits, criteria, and legal restrictions pertaining to environmental contaminants is most useful in the preliminary determination of pollutants prioritization and desired goals or range of limitations in the environment. A thorough review of all recent pertinent literature, including Federal Register, Environment Reporter, and Code of Federal Regulations, was made by an EPA contract granted to Research Triangle Institute, Research Triangle Park, North Carolina.[11] Some emphasis has also been placed on those regulations that are associated with fossil fuels processes, such as the recommended standards for gasification plants.

3.1 MULTIMEDIA ENVIRONMENTAL GOALS (MEG's)

The establishment of MEG's as estimates of desirable ambient and emission levels of control is an integral part of EPA's environmental assessment approach. As a result, Minimum Acute Toxicity Effluent (MATE) values to serve as MEG's for each chemical substance on the MEG's master list were established in the absence of existing or proposed federal guidelines. The MATE values are estimated levels of effluent contaminants considered to be safe for short-term exposures. The MATE values provide an increasingly useful tool for comparison in environmental assessment.

The objectives in the use of MEG's are two-fold: (1) to compare environmental pollutant loadings from specific sources to MEG's; and (2) to provide sufficient information for decision making. The use of MEG's shall include ranking of waste streams, establishing priorities for sampling and analysis, control options recommendation, and the provision of a basis for the establishment or revision of standards and regulations.

The relationship among various functional environmental assessment areas is depicted in Figure 1-1.

Multimedia Environmental Goals (MEG's) are levels of contaminants or degradants (in ambient air, water, or land or in emissions or effluents conveyed to ambient media) that are judged to be: (1) appropriate for preventing certain negative effects in the surrounding populations or ecosystems; or (2) representative of the control limits achievable through technology.

A master list of more than 600 chemical substances and physical agents has been compiled using selection factors prescribed by EPA. Primary emphasis has been placed on contaminants from fossil fuels processes (particularly coal gasification and liquefaction), and the master list has been compiled largely on the basis of the literature pertinent to these processes. Process streams were characterized both qualitatively and quantitatively, wherever possible, to provide insight for selecting substances likely to be present but not mentioned specifically in the process literature.

Three levels of priority were assigned to the selection factors to determine what substances, of all possible chemical substances and physical agents that might be described as environmental contaminants, would be entered on the master list for MEG's. The selection factors were categorized into three groups - primary, secondary, and tertiary.

The primary group includes pollutants associated with fossil fuels processes. All individual substances or classes of substances known or suspected to be present in the emissions or effluents from fossil fuels processes must appear on the master list.

Substances receiving secondary consideration include those for which federal standards exist or have been proposed (ambient, emission, or occupational) or those for which a Threshold Limit Value (TLV) has been established or an LD_{50} has been reported. Also included in the secondary group are substances which have been listed as suspected carcinogens or have appeared on the EPA Consent Decree List. Compounds that meet any one of the four secondary selection factors and are representative of a class of compounds associated with fossil fuels processes must appear on the master list.

If the substance is present as a pollutant in the environment, or if it has been identified as being highly toxic, it will receive tertiary or optional consideration. Consideration for inclusion in the master list is also given to certain additional pollutants, not necessarily associated with fossil fuels processes, provided they satisfy either of the tertiary selection factors.

A detailed documentation regarding MEG's and MATE's was prepared by Research Triangle Institute for EPA. A sample MEG's chart for 2-aminonaphthalene is included (Table 3-1).

3.1.1 Emission Level Goals

Emission level goals presented in the top half of a MEG's chart pertain to gaseous emissions to the air, aqueous effluents to water, and solid waste to be disposed to land. These goals may have technological or ambient factors as their bases. Technological factors refer to the limitations placed on control levels by technology, either existing or developing (i.e., equipment capabilities or process parameters). The standards of performance for new stationary sources provides an example of promulgated emission level goals based on technology.

Since there is obviously a relationship between contaminant concentrations in emissions and the presence of these contaminants in ambient media, it is imperative to consider ambient factors when establishing emission level goals. Ambient factors included in the MEG's chart as criteria for emission level goals include minimum acute toxicity effluents, ambient level goals, and elimination of discharge. Minimum Acute Toxicity Effluents (MATE's) are concentrations of pollutants in undiluted emission streams that would not adversely affect those persons or ecological systems exposed for short periods of time.

In applying the MEG charts, one problem reported is that, for some potential pollutants, such as benzo-a-pyrene, the MATE value given is below the detection limit for the substance. Consequently, it is impossible to determine whether a sample concentration is above or below the MATE value. Another problem is that MATE's have not yet been established for some species that may be collected in Level 1 sampling and analysis. Some MATE values for water and land do not make sense because they are based on the MATE value for air. An example is calcium, whose MATE value for land, which is based on the air MATE, seems unrealistically low.

MULTIMEDIA ENVIRONMENTAL GOALS

X
10C
2-AMINONAPHTHALENE

Emission Level Goals

	I. Based on Best Technology		II. Based on Ambient Factors				
	A. Existing Standards	B. Developing Technology	A. Minimum Acute Toxicity Effluent		B. Ambient Level Goal*		C. Elimination of Discharge
	NSPS, BPT, BAT	Engineering Estimates (R&D Goals)	Based on Health Effects	Based on Ecological Effects	Based on Health Effects	Based on Ecological Effects	Natural Background*
Air, g/m^3 (ppm Vol)			1.65E2		0.4		
Water, g/l (ppm Wt)			2.5E3	1.0E2	6	50	
Land, g/g (ppm Wt)			5.0E0	2.0E-1	0.012	0.1	

*To be multiplied by dilution factor.

Ambient Level Goals

	I. Current or Proposed Ambient Standards or Criteria		II. Toxicity Based Estimated Permissible Concentration		III. Zero Threshold Pollutants Estimated Permissible Concentration
	A. Based on Health Effects	B. Based on Ecological Effects	A. Based on Health Effects	B. Based on Ecological Effects	Based on Health Effects
Air, g/m^3 (ppm Vol)			59		0.4
Water, g/l (ppm Wt)			291	50	6
Land, g/g (ppm Wt)			0.6	0.1	0.012

Table 3-1 - Sample MEG Chart

Source: Cleland, J. G. and G. L. Kingsbury, "Summary of Key Federal Regulations and Criteria for Multimedia Environmental Control," Draft, 68-02-1325, Research Triangle Institute, June, 1977.

3.1.2 Ambient Level Goals

The ambient level goals are Estimated Permissible Concentrations (EPC's) of pollutants in emission streams which, after dispersion, will not cause the level of contamination in the ambient receiving medium to exceed a safe continuous exposure concentration. The Elimination of Discharge (EOD) refers to concentrations of pollutants in emission streams which, after dilution, will not cause the level of contamination to exceed levels measured as "natural background."

Although technology-based emission level goals are highly source specific, goals based on ambient factors can be considered universally applicable to discharge streams for any industry. The emission level goals correspond to the most stringent ambient level goals (dilution factor to be applied) appearing in the MEG chart, regardless of source of emission.

The lower half of a MEG chart is designed to present three classifications of ambient level goals; all of these goals describe estimated permissible concentrations (EPC's) for continuous exposure. The ambient level goals presented in the chart are those based on current or proposed federal ambient standards or criteria, toxicity (acute and chronic effects considered), and carcinogenicity or teratogenicity (for zero threshold pollutants). The term "zero threshold pollutants" is used to distinguish contaminants demonstrated to be potentially carcinogenic or teratogenic. The concept of thresholds is based on the premise that there exists for every chemical substance some defineable concentration below which that chemical will not produce a toxic response in an exposed subject. The existence of thresholds for carcinogens, teratogens, and mutagens has been widely debated and is still unresolved.

Existing or proposed federal standards, criteria, or recommendations are acknowledged as previously established goals and have been utilized wherever applicable. For those substances not addressed by current guidelines, consideration in arriving at MEG's has been given to: (1) established or estimated human threshold levels; (2) acceptable risk levels for lifetime exposure to suspected carcinogens or teratogens; (3) degrees of contamination considered reasonable for protection of existing ecosystems; (4) cumulative potential in aquatic organisms, livestock, and vegetation; and (5) hazards to human health or to ecology induced by short-term exposure to emissions. It is recognized that there are several other criteria pertinent to MEG's that have not been incorporated into the methodology developed thus far (for example, quality of the receiving media before introduction of the substance, characteristics of transport and dispersion of emissions, consideration of location and abundance of sources emitting a given pollutant, numbers of populations affected, synergisms, antagonisms, and other secondary pollutant associations). Research is needed before more refined models of estimation can be developed to allow inclusion of these criteria.

Three distinct aspects of MEG's methodology development have been addressed so far. These are:

1. Assembling and collating all existing or proposed federal guidelines pertinent to each chemical substance on the master list.
2. Defining models to translate empirical data into EPA's methodology, e.g., estimated permissible concentrations for continuous exposure to chemical toxicants in air, water, and land.
3. Defining models to translate empirical data into values describing MATE's (minimum acute toxicity effluents) safe for short-term exposure; such effluents may be gases, liquids, or solids.

3.2 NSPS SUPPORT RESEARCH DATA BASE FOR EMISSION STANDARDS

One major product of the environmental assessment effort will be the development of a research data base adequate for recommending emission standards for residual fuel oil utilization systems used in power generation or industrial steam generation. The research data base will include waste stream analysis data which constitute best current practice, including characterization of the available control technology, and health/ecology-based (ambient-level-goals-related) emission level goals.

An effluent standard is a limit on the amount or concentration of a pollutant emitted from a source. The concentration of pollutant in the effluent may be stated subjectively, in terms of its appearance to the eye or its odor, or objectively, in terms of its weight or volume. Emission standards may be derived from ambient quality considerations; process, fuel, and equipment considerations, or both. Effluent standards sometimes reflect economic, sociological, and political considerations in addition to those which are technological. In some cases, the technological ability to control certain pollutants is available but is not implemented for economic, sociological, or political reasons. However, despite considerable economic, sociological, and political pressure to more stringently regulate certain emissions, adequate technological ability is often lacking.

The major rationales for developing effluent standards have been based upon the following factors: (1) ambient quality; (2) ambient quality standards; (3) number and location of sources; and (4) meteorology and topography. The most common rationale for developing effluent limits for stationary sources is the application of best practicable means for control. Under this rationale, the degree of emission limitation achievable at the best designed and operated installation in a category sets the emission limits for all other installations of that category. The procedures generally being used in setting effluent standards involve derivations from ambient quality standards, from ambient background concentration, including the roll-back approach, and from process and equipment consideration.

There have been no specific regulations or guidelines officially issued regarding emissions from residual fuel oil utilization processes. Two applicable ones are the "Recommended Standards Support" regarding coal conversion involving Lurgi coal gasification process, and "Recommended Standards of Performance" for coal gasification process. These informal standards of performance were recommended by EPA and issued by the Office of Air Quality Planning and Standards (OAQPS).

To ensure adequate database development in supporting effluent standards setting, the steps in the environmental assessment methodology developed by EPA(5) will be followed in our residual fuel oil utilization environmental assessment work. The steps are summarized as follows:

Step 1. Identification of current technology and environmental background, including development of "the universe of potential pollutants."

Step 2. Development of environmental objectives via the Multimedia Environmental Goals (MEG's) Chart, which is preceded by preliminary pollutant prioritization.

Step 3. Analysis of emissions from operating residual fuel oil utilization processes.

Step 4. Assessment of existing control technology based on emission stream composition results from Steps 1 and 3.

Step 5. Analysis of environmental control alternatives, using Source Analysis Models (SAM's).

Step 6. Identification of further data and technology needs, including review of logical aspects of design of a control technology development program.

The ambient background information is the backbone of effluent standards setting, as well as the starting point of any environmental assessment work. A vast amount of information and data regarding ambient background has been collected and published over the years. There is more unpublished information scattered around in research institutes, universities, private industries, and governmental agencies.

To collect, evaluate, and process data on ambient concentrations in gaseous liquid, and solid media for noncriteria chemical substances, EPA initiated and granted a noncriteria ambient baseline data contract to Research Triangle Institute, Research Triangle Park, North Carolina.

A computer search of five files has been initiated. Files include: APTIC, WRA, NTIS, STOREX, and Pollution Abstracts. Over 100 reprints covering 350 chemicals have been ordered. These will serve as the basis for input into the data base being developed by Research Triangle Institute with assistance from the Midwest Research Institute.

Air Pollution

Although no effluent regulations or guidelines have been issued specifically for residual oil utilization processes, certain general emission guidelines are applicable. National primary and secondary ambient air quality standards have been promulgated which set limits on the ambient concentrations of sulfur oxides, particulate matter, carbon monoxide, photochemical oxidants, hydrocarbons, and nitrogen dioxide. The regulations call for prevention of significant deterioration (PSD), thus setting a limit on the total pollutant level from all sources in a given area, including residual oil utilization processes.

New source performance standards (NSPS) have been established for fossil-fuel fired steam generators for sulfur oxides, nitrogen oxides, and particulate matter. "Fossil fuel," as defined in the regulations, means natural gas, petroleum, coal, and any form of solid, liquid, or gaseous fuel derived from such materials, and would include residual oil.

State implementation plans (SIP's) are required by law for each state. SIP's provide the mechanism within each state for meeting national ambient goals, using reasonable available control technology.

The national emission standards for hazardous air pollutants (NESHAP) apply to specific industries likely to generate asbestos, beryllium, mercury, and vinyl chloride. Although NESHAP limits are not legally enforceable standards for power generation facilities (such as residual oil utilization processes), they do serve as emission guidelines.

In non-attainment areas, the desired effluent goal for any point source, including residual oil utilization facilities, is the lowest achievable emission rate. No standards have been set for some potential air pollutants, such as oxides and sulfates of trace metals.

Water Pollution

One source of effluent guidelines for water pollutants is the Resource Conservation and Recovery Act (RCRA). The National Pollutant Discharge Elimination System (NPDES) permits, licenses (such as for ocean dumping), pretreatment standards, and state guidelines also set limits on pollutant discharges in wastewater.

The Safe Drinking Water Act provides additional ambient guidelines, and the new source performance standards for steam electric power generating facilities provide effluent standards for pollutants such as total suspended solids (TSS) and oil and grease. As in the case of air pollutants, many potential water-borne pollutants such as heavy metals and organics are presently without effluent standards.

Controlling waterborne toxic and hazardous chemicals resultant from the residual fuel utilization processes will be far more complicated than controlling the conventional wastewater parameters, such as BOD, pH, TSS, etc. Based on EPA's experience in implementing water and hazardous materials programs of PL 92-500, Best Available Technology (BAT) is still the best approach. BAT calls for heavy reliance on in-process controls and on advanced technology as the most appropriate means for dealing with the majority of toxic discharges. The nature of the toxics problem is so pervasive that the most effective approach in dealing with it is on an industry-by-industry basis. EPA's studies over the past two years have identified large numbers of pollutants that have known or strongly suspected toxic effects. Many are carcinogenic. The most practical way of solving such a problem is to examine each industry category or subcategory. In this manner, control options can be developed that deal most effectively with the entire wastestream of an industry. This is the approach called for in BAT. As new technology is developed, what was best practicable means in 1978 may be short of the best attainable in 1980. Since there is a moving target, emissions goals may have to be set at various time periods; and, means must be provided administratively to provide adequate incentive for continued technology development.

Solid Wastes

The Resource Conservation and Recovery Act (RCRA) calls for state plans for development of solid waste disposal practices which comply with federal guidelines. Solid waste criteria, identification methods, and listing of hazardous wastes are available in the RCRA.

Toxic Substances

Recent EPA actions have officially endorsed toxic effluent standards and established effluent limitations requirements for selected toxicants. Three different kinds of regulations are anticipated for ten classes of industries by December 1979. These regulations include effluent limitations, pretreatment standards, and new source performance standards. A permit procedure will be incorporated into the National Pollutant Discharge Elimination System (NPDES) for certain toxic effluents. The NPDES permits will have to be reviewed annually to incorporate new toxic limitations.

The EPA is presently undertaking a major assessment of toxic pollutants discharged by industrial sources in order to review and revise, if necessary, the effluent limitations within five years. A criteria has been established for assigning priority to specific compounds, which in general are thought to pose a threat to human health as a result of exposure. As a result of the EPA work, the following regulations will be put into effect:

1) Revised effluent limitations based on the Best Available Technology Economically Achievable (BATEA) to be met by 1983;
2) Revised New Source Performance Standards (NSPS) based on the Best Available Demonstrated Control Technology (BADCT) to be met by new source industrial dischargers;
3) Revised pretreatment standards for existing dischargers to any publicly-owned treatment facility; and
4) Revised pretreatment standards for new sources for new dischargers to publicly-owned treatment facilities.

The EPA has scheduled completion dates for development of these regulations on an industry basis by December 1979. The EPA has recommended that the BATEA limitations not be regarded as high priority enforcement items until the toxic effluent guidelines become available after 1979.

The Toxic Substances Control Act (TOSCA) mandates registration and premanufacture notification for new chemical substances, and provides for testing of potential toxicants. Data on health and/or environmental effects of potential toxic substances, collected via TOSCA-authorized testing, serves as a basis for standards support.

Radiation

Radiation is not foreseen as a major problem with residual oil utilization processes. Currently, there are no applicable regulations; however, EPA's radiation office is available to provide guidance, should it become necessary.

Noise

Noise from residual oil utilization processes is presently unregulated. Establishment of a data base for noise regulation is presently underway at EPA's office of noise.

3.3 SUMMARY

Concern with the current environmental background is focussed on ambient and emission level goals for pollutants related to residual oil utilization processes. Multimedia Environmental Goals (MEG's) have been established as estimates of desirable ambient and emissions levels of control, and Minimum Acute Toxicity Effluents (MATE's) have been established in the absence of existing or proposed federal guidelines, and serve as a valuable tool for emissions comparisons.

Emission level goals are based on both technological factors and ambient factors, and are highly source-specific. Ambient level goals are universally applicable to discharge streams from any industry.

Research is needed for refinement of the MEG's to incorporate important criteria that are presently not considered in MEG's development.

Effluent guidelines are being developed in the form of a research data base adequate for recommending emissions standards. The most common rationale for developing effluent limits for stationary sources is the application of best practicable control technology. The ultimate basis for effluent standards setting is ambient background information.

Toxic effluent standards have recently been endorsed by EPA actions, and criteria have been established for assigning priority to specific compounds.

SECTION 4

ENVIRONMENTAL DATA ACQUISITION

The major goal of the Environmental Data Acquisition subtask is a comprehensive waste stream characterization for each residual oil utilization process. The waste stream characterizations will be used to compare the environmental impacts of each process.

Emissions loadings for each process can be established by two methods: sampling/analysis and theoretical engineering analysis. Some weighted combination of both sets of results will most accurately predict the actual emissions. Sampling and analysis results are valuable because they are taken directly from operating facilities. However, neither equipment nor methods for sampling and analysis are entirely accurate. For example, the SASS train is non-isokinetic and has problems with metal contamination. Inorganics have been found to dissolve in condensate/water rather than in the impingers, as originally designed.

Theoretical engineering analysis based on the thermodynamics and kinetics of the process serves as a check on the sampling/analysis results and as a source of information for filling data gaps and estimating error in sampling/analysis results.

4.1 EMISSIONS INVENTORY

In order for projected emissions loadings for each residual oil utilization process to be compared with each other, the emissions must be based on the same feedstock. Actual residual oil compositions, however, vary widely from oil to oil. For typical residual oils, sulfur concentrations range from 1% to 6% by weight; and, nitrogen varies from 1000 to 6000 ppm by weight. Trace element concentrations may vary over an even broader range. Of the 60 or so detectable trace species in residual oil, vanadium and nickel are two of the most important indicators of metal content. Vanadium concentrations are found as low as 10 ppm by weight and as high as 300 ppm by weight, typically, while nickel varies from less than 10 to at least 80 ppm by weight. The wide variation in residuum constituents is due to the equally wide variation in crude oils imported into the U.S.A. from sources around the world and the common refinery practice of blending the bottoms from several different crudes into one final residual oil.

To maintain comparability between the different residual oil utilization technologies, a composite oil analysis has been developed, based on a weighted average of U. S. crudes, which is representative of a "typical" residual oil feedstock (Table 4-1). By using this composite oil analysis as a basis for projected emissions loadings, the air, water, and land pollutant removal efficiencies can be readily compared between processes.

It is important to remember that the projected emissions based on the composite oil analysis will, of course, be average emission rates and that actual emissions from operating plants will depend on the composition of the oil being fired. To establish the range of possible emissions, projections based on dirtier-than-average and cleaner-than-average resids will be defined. The major variables are sulfur and trace metals content.

For the CAFB and FGD processes, the other major source of potential pollutants is the sorbent used. The non-regenerable or "throwaway" FGD process under study employs limestone as the sorbent. The assumed limestone composition to be used for input to FGD emission calculations is taken from the ERCA (Esso Research Center, Abingdon) analysis of BCR 1359, shown in Table 4-2, since it is comprehensive, recent, and reliable.

The regenerable FGD process under study employes a magnesium oxide slurry. The exact nature of MgO impurities as supplied to a magnesium oxide FGD system has not been defined as of yet. So far, literature search has failed to find a complete trace element analysis of MgO slurry; thus, sampling and analysis may be the only source of obtaining this data.

The two viable sorbents for the CAFB process are limestone and dolomite; thus, emissions based on both options are of concern. The BCR 1359 limestone used as a basis for FGD emission calculations is also used as a basis for the CAFB calculations. For CAFB with dolomite as the sorbent, the ERCA analysis

TABLE 4-1. AVERAGE RESIDUAL OIL COMPOSITE ANALYSIS (1)

Element	Concentration(2)	Element	Concentration(2)
Carbon	85.1%	Uranium	0.7 PPM
Hydrogen	11.2%	Antimony	0.44 PPM
Sulfur	2.5%	Boron	0.41 PPM
Nitrogen	4400 PPM	Gallium	0.4 PPM
Vanadium	160 PPM	Indium	0.3 PPM
Nickel	42.2 PPM	Silver	0.3 PPM
Potassium	34 PPM	Germanium	0.2 PPM
Sodium	31 PPM	Thallium	0.2 PPM
Iron	18 PPM	Zirconium	0.2 PPM
Silicon	17.5 PPM	Strontium	0.15 PPM
Calcium	14 PPM	Bromine	0.13 PPM
Magnesium	13 PPM	Fluorine	0.12 PPM
Chlorine	12 PPM	Ruthenium	0.10 PPM
Tin	6.2 PPM	Tellurium	0.1 PPM
Aluminum	3.8 PPM	Cesium	0.09 PPM
Lead	3.5 PPM	Beryllium	0.08 PPM
Copper	2.8 PPM	Iodine	0.06 PPM
Cadmium	2.27 PPM	Lithium	0.06 PPM
Cobalt	2.21 PPM	Mercury	0.04 PPM
Rubidium	2 PPM	Tantalum	0.04 PPM
Titanium	1.8 PPM	Rhodium	0.03 PPM
Manganese	1.33 PPM	Gold	0.02 PPM
Chromium	1.3 PPM	Platinum	0.02 PPM
Barium	1.26 PPM	Scandium	0.02 PPM
Zinc	1.26 PPM	Bismuth	0.01 PPM
Phosphorus	1.1 PPM	Cerium	0.006 PPM
Molybdenum	0.90 PPM	Tungsten	0.004 PPM
Arsenic	0.8 PPM	Hafnium	0.003 PPM
Selenium	0.7 PPM	Yttrium	0.002 PPM
		Niobium	0.001 PPM

Note: (1) based on U. S. crudes, including imports and domestic sources

(2) concentration by weight

TABLE 4-2. ANALYSIS OF LIMESTONE USED BY ERCA[1]

Element	Concentration, by weight	Element	Concentration, by weight
Ca	71.5%	Sb[3]	< 10 ppm
Mg[2]	0.2 - 2%	I[2]	1 - 10 ppm
Si[2]	600 - 6000 ppm	P[2]	1 - 10 ppm
Al[2]	200 - 2500 ppm	Ti[2]	0.6 - 6 ppm
Fe[2]	200 - 2000 ppm	Te[3]	2 ± 0.4 ppm
Sr	100 - 1000 ppm	Cr[3]	2 + 0.2 ppm
K[2]	100 - 1000 ppm	La[2]	0.3 - 3 ppm
Ba[2]	30 - 300 ppm	Co[2]	0.3 ± 0.01 ppm
Cl[2]	10 - 100 ppm	V[2]	0.06 - 0.6 ppm
Na[2]	10 - 100 ppm	Surface O[4]	49.5%
Ni[2]	< 50 ppm	Surface C[4]	38.9%
Cd or In[3]	29 + 6 ppm	Surface Ca[4]	11.6%
Mn[3]	22 ± 1 ppm	$Co_3{}^{=}/C$[4]	0.5

Notes:
1. All results except surface elements and $Co_3{}^{=}/C$ from ERCA
2. Atomic Absorption (AA) spectroscopy
3. Neutron Activation Analysis (NAA) performed by the U.K. Atomic Energy Establishment, Harwell
4. Electron Spectroscopy for Chemical Analysis (ESCA) by GCA Corporation

Source: Werner, et al., "Preliminary Environmental Assessment of the CAFB," EPA-600/7-76-017, October, 1976.

of Tymochtee dolomite is used. Although it does not include all trace elements, it is the most complete dolomite analysis readily available and does include all metal oxides above the ppm level, as well as vanadium, nickel, and sodium. Those trace elements which occur in dolomite in lesser quantities probably exist at levels nearly equal to their concentration in the BCR 1359 limestone and will be assumed as such.

The only other major process inputs are the hydrogen and the catalyst for hydrodesulfurization. The hydrogen feed to HDS, produced in the crude oil cracking process, is greater than 99% pure. Any contamination is probably in the form of minute amounts of hydrocarbons. HDS catalysts for desulfurization of residual oil usually consist of an alumina or silica base, promoted with catalyst material such as molybdenum, cobalt, nickel, or some combination of these metals.

4.1.1 Theoretical Engineering Analysis

Computerized equilibrium calculations will be employed to predict trace species formation during combustion of residual oil. Equilibrium compositions of trace chemical compounds are determined by the free energy minimization method, based on the following input data: (1) elemental analysis of all feed materials (oil, air, and sorbent, where applicable); (2) process conditions (temperature and pressure); (3) a list of all compounds expected to be formed; (4) standard free energy of formation for each species at equilibrium conditions; and (5) the phase (solid, liquid, or gas) of each species at equilibrium.

As an aid in determining expected pollutant loadings in FGD effluents, the equilibrium calculations computer program will be used to determine combustion products from a residual oil-fired boiler, which will serve as input to the FGD scrubber system. Input to the computer program is based on the previously completed material balance for a $500MW_e$ scrubber system. At 20% excess combustion air, the resid flow to the boiler is 287,000 lb/hr, and the air flow is 4,680,000 lb/hr. Standard boiler conditions are assumed to be $2000^{o}K$ and 1.5 psig (1.1 atm.). The oil and air feeds are broken down by elements and combined to give the total flow rate for each element into the boiler. The results are listed on Table 4-3.

TABLE 4-3. EQUILIBRIUM CALCULATION INPUTS BASED ON COMPOSITE OIL

	Total Mass Flow Rates, g/sec.			
Element	CAFB (Gasifier)	FGD (Boiler)	POX (Gasifier)	HDS (Boiler)
Nitrogen	7.98×10^{4}	4.41×10^{5}	2.05×10^{5}	3.78×10^{5}
Oxygen	2.53×10^{4}	1.40×10^{5}	6.50×10^{4}	1.04×10^{5}
Carbon	3.38×10^{4}	3.09×10^{4}	3.95×10^{4}	2.49×10^{4}
Hydrogen	4.56×10^{3}	4.68×10^{3}	5.48×10^{3}	3.74×10^{3}
Argon	1.36×10^{3}	7.55×10^{3}	3.50×10^{3}	5.61×10^{3}
Sulfur	9.92×10^{2}	9.04×10^{2}	1.16×10^{3}	2.92×10^{1}
Vanadium	6.35×10^{0}	5.79×10^{0}	7.42×10^{0}	2.34×10^{-1}
Nickel	1.94×10^{0}	1.53×10^{0}	1.96×10^{0}	6.2×10^{-2}
Potassium	4.22×10^{0}	1.23×10^{0}	1.58×10^{0}	5.0×10^{-2}
Sodium	1.52×10^{0}	1.12×10^{0}	1.44×10^{0}	4.5×10^{-2}
Iron	6.46×10^{0}	6.51×10^{-1}	8.34×10^{-1}	2.6×10^{-2}
Silicon	1.79×10^{1}	6.33×10^{-1}	8.11×10^{-1}	2.6×10^{-2}
Calcium	3.73×10^{3}	5.06×10^{-1}	6.49×10^{-1}	2.0×10^{-2}
Magnesium	5.79×10^{1}	4.70×10^{-1}	6.03×10^{-1}	1.9×10^{-2}
Chlorine	7.63×10^{-1}	4.34×10^{-1}	5.56×10^{-1}	1.8×10^{-2}
Tin	2.46×10^{-1}	2.24×10^{-1}	2.87×10^{-1}	9.1×10^{-3}
Aluminum	7.20×10^{0}	1.38×10^{-1}	1.76×10^{-1}	5.6×10^{-3}
Lead	1.37×10^{-1}	1.27×10^{-1}	1.62×10^{-1}	5.1×10^{-3}
Copper	1.11×10^{-1}	1.01×10^{-1}	1.30×10^{-1}	4.1×10^{-3}
Cadmium	2.42×10^{-1}	8.2×10^{-2}	1.05×10^{-1}	3.3×10^{-3}
Cobalt	8.9×10^{-2}	8.0×10^{-2}	1.02×10^{-1}	3.2×10^{-3}
Rubidium	7.9×10^{-2}	7.2×10^{-2}	9.3×10^{-2}	2.9×10^{-3}
Titanium	8.9×10^{-2}	6.5×10^{-2}	8.3×10^{-2}	2.6×10^{-3}
Manganese	1.68×10^{-1}	4.8×10^{-2}	6.2×10^{-2}	1.9×10^{-3}
Chromium	6.2×10^{-2}	4.7×10^{-2}	6.0×10^{-2}	1.9×10^{-3}
Barium	9.12×10^{-1}	4.6×10^{-2}	5.8×10^{-2}	1.8×10^{-3}
Zinc	5.0×10^{-2}	4.6×10^{-2}	5.8×10^{-2}	1.8×10^{-3}
Phosphorous	7.2×10^{-2}	4.0×10^{-2}	5.1×10^{-2}	1.6×10^{-3}
Molybdenum	3.6×10^{-2}	3.3×10^{-2}	4.2×10^{-2}	1.3×10^{-3}
Arsenic	3.2×10^{-2}	2.9×10^{-2}	3.7×10^{-2}	1.2×10^{-3}

(continued)

TABLE 4-3 (continued)

	Total Mass Flow Rate, g/sec.			
Element	CAFB (Gasifier)	FGD (Boiler)	POX (Gasifier)	HDS (Boiler)
Selenium	2.8×10^{-2}	2.5×10^{-2}	3.2×10^{-2}	1.0×10^{-3}
Uranium	2.8×10^{-2}	2.5×10^{-2}	3.2×10^{-2}	1.0×10^{-3}
Antimony	7.0×10^{-2}	1.6×10^{-2}	2.0×10^{-2}	6×10^{-4}
Boron	1.6×10^{-2}	1.5×10^{-2}	1.9×10^{-2}	6×10^{-4}
Gallium	1.6×10^{-2}	1.4×10^{-2}	1.9×10^{-2}	6×10^{-4}
Indium	1.63×10^{-1}	1.1×10^{-2}	1.4×10^{-2}	4×10^{-4}
Silver	1.2×10^{-2}	1.1×10^{-2}	1.4×10^{-2}	4×10^{-4}
Germanium	7.9×10^{-3}	7.2×10^{-3}	9.3×10^{-3}	3×10^{-4}
Thallium	7.9×10^{-3}	7.2×10^{-3}	9.3×10^{-3}	3×10^{-4}
Zirconium	7.9×10^{-3}	7.2×10^{-3}	9.3×10^{-3}	3×10^{-4}
Strontium	6.0×10^{-3}	5.4×10^{-3}	7.0×10^{-3}	2×10^{-4}
Bromine	5.2×10^{-3}	4.7×10^{-3}	6.0×10^{-3}	2×10^{-4}
Fluorine	4.8×10^{-3}	4.3×10^{-3}	5.6×10^{-3}	2×10^{-4}
Ruthenium	4.0×10^{-3}	3.6×10^{-3}	4.6×10^{-3}	1×10^{-4}
Tellurium	1.4×10^{-2}	3.6×10^{-3}	4.6×10^{-3}	1×10^{-4}
Cesium	3.6×10^{-3}	3.3×10^{-3}	4.3×10^{-3}	1×10^{-4}
Beryllium	3.2×10^{-3}	2.9×10^{-3}	3.7×10^{-3}	1×10^{-4}
Iodine	3.1×10^{-2}	2.2×10^{-3}	2.8×10^{-3}	9×10^{-5}
Lithium	2.4×10^{-3}	2.2×10^{-3}	2.8×10^{-3}	9×10^{-5}
Mercury	1.6×10^{-3}	1.5×10^{-3}	1.9×10^{-3}	6×10^{-5}
Tantalum	1.6×10^{-3}	1.5×10^{-3}	1.9×10^{-3}	6×10^{-5}
Rhodium	1.2×10^{-3}	1.1×10^{-3}	1.4×10^{-3}	4×10^{-5}
Gold	8×10^{-4}	7×10^{-4}	9×10^{-4}	3×10^{-5}
Platinum	8×10^{-4}	7×10^{-4}	9×10^{-4}	3×10^{-5}
Scandium	8×10^{-4}	7×10^{-4}	9×10^{-4}	3×10^{-5}
Bismuth	4×10^{-4}	4×10^{-4}	5×10^{-4}	1×10^{-5}
Cerium	2×10^{-4}	2×10^{-4}	3×10^{-4}	9×10^{-6}
Tungsten	2×10^{-4}	1×10^{-4}	2×10^{-4}	6×10^{-6}
Hafnium	1×10^{-4}	1×10^{-4}	1×10^{-4}	4×10^{-6}
Yttrium	8×10^{-5}	8×10^{-5}	9×10^{-5}	3×10^{-6}
Niobium	4×10^{-5}	4×10^{-5}	5×10^{-5}	1×10^{-6}
Lanthanum	8.6×10^{-3}	--	--	--

Equilibrium calculations are to be performed on the three major unit operations of the CAFB process: gasification of the resid feed, regeneration of spent sorbent, and combustion of the clean regenerator product gas in a boiler. Inputs to the computer program for gasification based on the material balance are 315,000 lb/hr of resid, 41,400 lb/hr of limestone, and 845,327 lb/hr of combustion air (about 22% of stoichiometric combustion air). Gasification conditions are taken as 1140°K and 1.5 psig (1.1 atm.).

Results of the equilibrium calculations for the gasifier will be evaluated using available field data and engineering judgment to determine what fraction of the generated pollutants are captured in the sorbent (and subsequently transferred to the regenerator) and what fraction are emitted with the product gas (which is used as boiler feed). The sorbent composition will then be used as input to the computerized equilibrium calculations for determination of regenerator products, and the product gas composition will be used as input to the boiler equilibrium calculations to determine boiler flue gas pollutant loadings. Regenerator conditions are 1310°K and 1.5 psig (1.1 atm.), and boiler conditions are 2000°K and 1.5 psig (1.1 atm.). Inputs for gasifier calculations are listed by element on the input sheet, but inputs for regenerator and boiler calculations cannot be determined until the gasifier results are available. Factors for converting gasifier effluent results to input data for regenerator and boiler calculations are being developed. Air/fuel ratio in the boiler is 2.13, and air/sorbent ratio in the gasifier is 0.09. Conditions and air flows are based on operating experience at the ERCA pilot plant.

Gasifier, regenerator, and boiler calculations will be repeated using dolomite, instead of limestone, as the sorbent. Inputs for the dolomite calculations have not been prepared due to lack of adequate dolomite trace element analyses.

Emissions from the partial oxidation gasifier will be estimated by computerized equilibrium calculations. Feed rates of 361,590 lb/hr of resid and 2,169,539 lb/hr of air (45% of stoichiometric combustion air) will be used, as established in the material balance for a $500MW_e$ capacity boiler. Typical operating conditions for the gasification process are 1650°K and 365 psia (25 atmospheres). However, the computer program is only valid for pressures up to 10 atmospheres, so a run will be made at that pressure; and, engineering judgment will be used to estimate pollutant generation at 25 atmospheres.

The gasifier products are split into two streams: cleaned low-Btu gas and carbon slurry. The composition of the cleaned gas will be established by subtracting from the equilibrium products the soot and ash expected to be entrained in the carbon slurry. The gasifier product gas elemental composition will then be used as input to equilibrium calculations for the boiler which follows the gasifier. At present, no data have been found on combustion air requirements specifically for POX product gas combustion; but, if the gas composition can be assumed to be similar to CAFB product gas, then combustion air is probably about 62% of stoichiometric air. Typical boiler conditions are taken as 2000°K and 1.5 psig (1.1 atm.).

The elemental composition of HDS-processed residual oil cannot be determined by the computerized equilibrium calculations because the process temperatures are too low. The computer program will be helpful, however, to predict pollutant formation in a 500MW$_e$ boiler fired with hydrodesulfurized resid, provided the desulfurized resid composition can be estimated. Since no complete trace element analyses for hydrodesulfurized resid are available, the trace element concentrations have been estimated by applying a 95% demetallization factor (taken from actual data for Gulf IV HDS of Light Arabian residuum) to the input trace element concentrations in the composite residual oil analysis. Combustion conditions are assumed to be 2000°K and 1.5 psig (1.1 atm.) with 10% excess air. The desulfurized fuel oil flow to the boiler is 232,078 lb/hr, and the combustion air flow is 3,481,170 lb/hr.

Computerized equilibrium calculations have not yet been performed for the specific processes under study, but the computer run matrix planned is shown in Table 4-4. Limited data are available, however, from a previously published report by Battelle.[23] The data include computer-predicted equilibrium products for the combustion of No. 6 fuel oil in a boiler. Computerized equilibrium calculations were performed for a No. 6 fuel oil having the composition shown in Table 4-5. Also shown is a comparison with the composite No. 6 fuel oil prepared by Catalytic. This composition indicates that the input oil composition used in the Battelle predictions is generally higher in trace metals content for those species considered but does not include all of the species included in the composite oil analysis.

TABLE 4-4. PLANNED COMPUTER RUN MATRIX

Run No.	Process	Unit	Oil	% Stoichiometric Air	Temperature	Pressure	Sorbent
1	FGD	Boiler	Composite	120	2000^oK	1.1 atm.	--
2	POX	Gasifier	Composite	45	1650^oK	10 atm.	--
2a	POX	Boiler	Composite	125	2000^oK	1.1 atm.	--
3	CAFB	Gasifier	Composite	22	1140^oK	1.1 atm.	Limestone
4	CAFB	Gasifier	Composite	22	1140^oK	1.1 atm.	Dolomite
3a	CAFB	Regenerator	Composite	.091*	1310^oK	1.1 atm.	Limestone
4a	CAFB	Regenerator	Composite	.091*	1310^oK	1.1 atm.	Dolomite
3b	CAFB	Boiler	Composite	125	2000^oK	1.1 atm.	Limestone
4b	CAFB	Boiler	Composite	125	2000^oK	1.1 atm.	Dolomite
5	HDS	Boiler	Composite	110	2000^oK	1.1 atm.	--

* Air/Stone Ratio

TABLE 4-5. A COMPARISON OF TYPICAL NO. 6 FUEL OIL COMPOSITIONS

Species	Battelle Program Input	Catalytic Composite
	% By Weight	
C	85.1	85.1
H_2	11.2	11.2
N_2	0.44	0.44
S_2	2.80	2.5
	ppm	
V	225	160
Ni	40	42.2
Na	18	31
Fe	262	18
Al	251	3.8
Si	188	17.5
Mg	20	13
Cr	16	1.3
Ca	13	14
Co	12	2.21
Ti	6	1.8
Cl		12
K		34
Sn		6.2
Pb		3.5
Cu		2.8
Cd		2.27
Rb		2.0
Others		< 2

Published results of Battelle's program runs for No. 6 fuel oil include equilibrium products of combustion at 1800°K, 800°K, 650°K, and 500°K, for both 10% and 2% excess air, as well as one run at 1800°K and -2% excess air. Results for 9 major species are shown in Figure 4-1 over the temperature range considered, for 10% and 2% excess air.

The amount of excess air makes very little difference in equilibrium product formation for the major species shown or for trace metal oxides and sulfates. The major effect of increased excess air is increased nitrogen oxide production and CO reduction.

Combustion temperature has very little effect on the formation of the major gaseous species N_2, CO_2, H_2O, and O_2; but, some of the compounds' concentrations vary dramatically between 500°K and 1800°K. Sulfur dioxide, nitrogen oxide, and carbon monoxide concentrations are greater by at least six orders of magnitude at the higher temperature, while SO_3 and H_2SO_4 formation is greater at the lower temperature.

Of the most abundant trace metal compounds formed, only SiO_2 and V_2O_5 remain constant over the entire temperature range. Aluminum, iron, and magnesium tend to form oxides at 800°K and above and sulfates at 650°K and below. Nickel and calcium form predominantly oxides at 1800°K but form mostly sulfates at the lower temperatures.

The predominant sodium compound at 1800°K is Na_2SiO_3, but sodium tends to favor sulfates below that temperature. Titanium and chromium, at minor concentrations, tend to form oxides across the temperature spectrum. Cobalt follows the general trend of forming oxides at the higher temperatures and sulfates at the lower temperatures. The metal sulfate distribution agrees well with the SO_2 distribution, which is highest at the higher temperatures where there are fewer metal sulfates, and lowest at the lower temperatures where there are more metal sulfates. The sulfur, then, reacts to form predominantly SO_2 at 1800°K; but, as the combustion temperature decreases, more of the sulfur is taken up in metal sulfates.

Emissions from Combustion Without Controls

The conditions for which computer data are available and most closely model actual residual oil-fired utility boiler operating conditions are 1800°K and

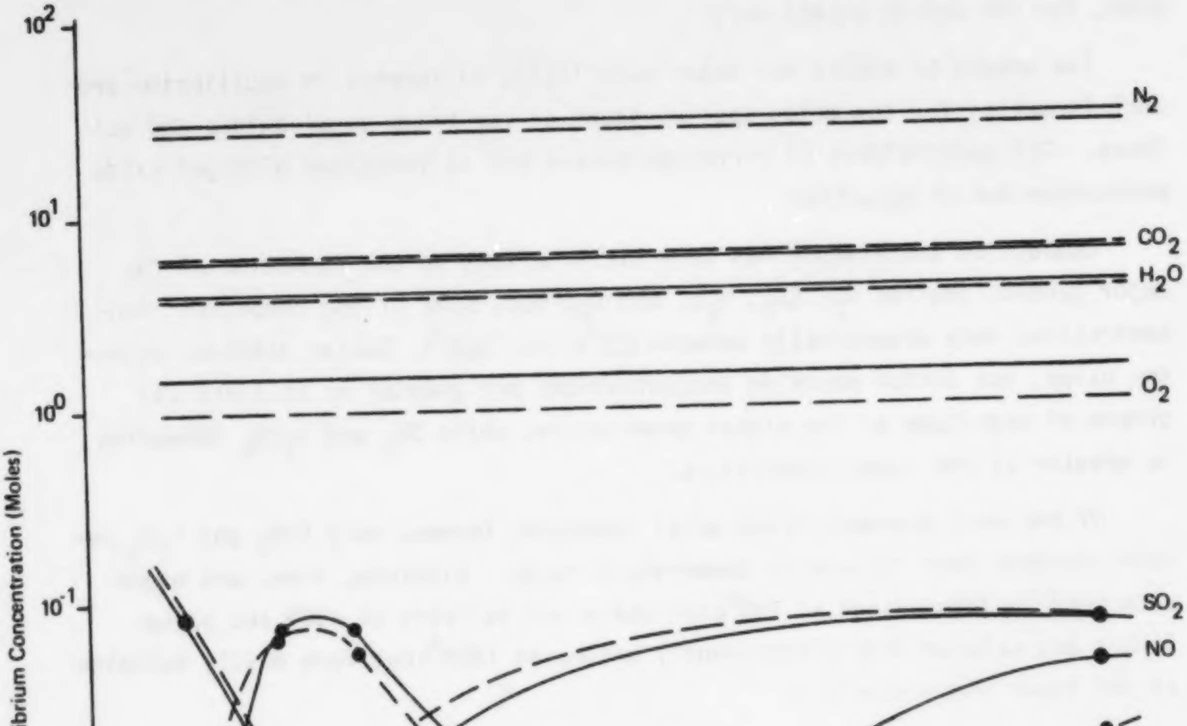

Figure 4-1 - Comparison of Effects of Excess Air on Products of Oil Combustion

10% excess combustion air (actual conditions generally vary between 1800-2200^{o}K[37] and 10-20% excess air).[2] Products of residual oil combustion in a utility boiler, then, based on the Battelle oil analysis of Table 4-5, should closely resemble the predicted equilibrium concentrations at those conditions. Solution chemistry kinetics are not expected to influence primary sulfate formation; and, in general, once the sulfates and nitrates are formed, they will not be destroyed (although some may be neutralized by adsorption on particulate material).[12]

Table 4-6 indicates typical slag composition for a residuum-fired boiler. At least part of each of the most abundant metal oxides appears to be captured in the boiler deposits. However, since portions of these deposits will be removed periodically via soot blowing, most of the pollutants will reach the atmosphere eventually. Thus, it is initially assumed that all of the predicted combustion products are emitted to the atmosphere.

The Battelle equilibrium calculations predict the emission levels of 74 species in the residual oil-fired boiler flue gas. Of those, the 21 species predicted to form in concentrations greater than one-tenth of their lowest MATE value are shown in Table 4-7(a), ranked by concentration/MATE value in order of their relative degree of potential hazard. Those of primary concern for control technologies are the 17 species predicted to be formed at concentrations greater than their MATE value. Table 4-7(b) lists those species predicted to exist in effluent concentrations less than one-tenth of their MATE values, and which are thus of secondary importance. Table 4-7(c) lists the 20 species for which no MATE's are available or easily estimated from others in the same category, and whose potential hazard is therefore undefined.

FGD Emissions

The two major effluents from limestone FGD systems are the treated flue gas and the spent sludge. Definitive trace species concentration data for the flue gas and the sludge are not yet available, but the major emissions are shown in Table 4-8.

All of the boiler effluent trace species of Tables 4-7(a), (b), and (c) exist in the condensed phase. At least 90% of the condensed phase species should be removed from the gas stream by the FGD mist eliminator. Thus, as a preliminary indicator of FGD performance with respect to trace species in the

TABLE 4-6. TYPICAL SLAG FROM BOILER FIRED WITH NO. 6 FUEL OIL(1)

	Oil Ash %	Superheater Deposit %
SiO_2	1.7	7.0
Al_2O_3	0.3	4.1
Fe_2O_3	3.8	5.8
CaO	1.7	4.5
MgO	1.1	2.5
NiO	1.9	1.1
V_2O_5	7.9	0.9
Na_2O	31.8	23.7
SO_3	42.3	46.4

Note: (1) from Chemical Engineering Handbook, 5th Edition, J. H. Perry, p. 9-10.

TABLE 4-7(a). EQUILIBRIUM CALCULATION - PREDICTED EMISSIONS FROM RESIDUAL OIL-FIRED BOILER WITHOUT CONTROLS(1)

	Fraction of Flue Gas (ppm)	MATE Health ug/m^3	MATE Ecology ug/m^3	Conc./MATE
V_2O_5	23.8	5×10^2	1.0	19,226
Cr_2O_3	1.3	1.0	--	1,052
SO_2 (g)	3.33×10^3	1.3×10^4	--	207
NiO	2.9	15	--	157
V_2O_4	.054	5×10^2	1.0	43.7
VO	.039	5×10^2	1.0	31.6
Cr	.030	1.0	--	24.3
V	.026	5×10^2	1.0	21.1
CO_2 (g)	1.85×10^5	9×10^6	--	16.7
CoO	.600	50	--	9.71
$NiSO_4$	.087	15(2)	--	4.70
CO (g)	185.0	4×10^4	1.2×10^5	3.74
$Ni(OH)_2$	.052	15(2)	--	2.81
Co_3O_4	.142	50(2)	--	2.30
Al_2O_3	28.1	1×10^4	--	2.27
SiO_2	20.8	1×10^4	--	1.68
Ni	.026	15	--	1.40
$CoSO_4$	.061	50(2)	--	.988
$CoCO_3$	.052	50	--	.842
$Co(OH)_3$	.042	50(2)	--	.680
Co	.034	50	--	.550

Notes: (1) All species in condensed phase unless otherwise noted.

(2) Estimated from other MATE's in same category.

TABLE 4-7(b). POLLUTANTS HAVING PROJECTED EMISSIONS LESS THAN ONE-TENTH OF THEIR MATE VALUE(1)

MgO
NO_2 (g)
TiO_2
$Al_2(SO_4)_3$
Fe
Na_2SO_3
Al
Na_2SO_4
Na_2CO_3
Ti_3O_5
Na_2O

Ti_2O_3
$NaOH$
N_2O (g)
$MgSO_4$
$Ni(NO_3)_2$
TiO
Ti
$Co(NO_3)_2$
C
Mg
$Co(OH)_2$

Si
Ca
Na
$Mg(NO_3)_2$
$Al(NO_3)_2$
H_2SO_4 (g)
HNO_3 (g)
COS (g)
N_2O_4 (g)
N_2O_5 (g)
CH_4 (g)

Note: (1) All species in condensed phase unless otherwise noted.

TABLE 4-7(c). COMPOUNDS IN PREDICTED EFFLUENT FOR WHICH NO MATE'S HAVE BEEN ESTABLISHED (1)

N_2(g)
H_2O (g)
O_2 (g)
NO (g)
H_2 (g)
SO_3 (g)
Fe_2O_3
Na_2SiO_3
CaO
$CaSO_4$
$Ca(OH)_2$
$NaNO_2$
$Fe(NO_3)_2$
$Ca(NO_3)_2$
$Ca(NO_2)_2$
$NaNO_3$
$CaCO_3$
$FeSO_4$
H_2SO_3 (g)
S_2 (g)

Note: (1) All species in condensed phase unless otherwise noted.

TABLE 4-8. TYPICAL FGD EMISSIONS

For a 2.5% S residual oil at 10% excess combustion air

Stack Gas Composition

	Per kg. #6 Fuel Oil	% Wt. of Total
CO_2	3.24 kg	20.5%
H_2O	.93 kg	5.9%
SO_2	.005 kg	.03%
N_2	11.34 kg	71.6%
O_2	.32 kg	2.0%
Total	15.835 kg	

Sludge Composition

	Per kg. #6 Fuel Oil	% of Total
$CaSO_4 \cdot 2H_2O$	.0484 kg	31.2%
$CaSO_3 \cdot 2H_2O$	.0658 kg	42.5%
Unreacted $Ca(OH)_2$	.0174 kg	11.2%
Unreacted $CaCO_3$	.0233 kg	15.0%
Total	.1549 kg	

effluent, it is assumed that 90% of the trace species in the boiler effluent are removed from the gas stream and taken up by the limestone slurry. Under steady-state conditions, then, 90% of the trace species are assumed to exit the system via the sludge.

The projected FGD stack gas trace species distribution of Table 4-9 is based on the assumption that 10% of the boiler emissions of Table 4-7(a) will escape the system and employs a factor of .974, which accounts for the increased flue gas mass due to make-up water evaporative losses, which exit via the stack. Table 4-9 shows only those trace species predicted to escape the boiler in quantities equal to or greater than their MATE values. About half of those are reduced to concentration/MATE ratios less than one, by the FGD system. Of those species which are still projected to exist in concentrations greater than their MATE value, four are vanadium compounds, two are of chromium, and one is of nickel. The CO_2 emission level is 16.3 times its MATE value, but the potential hazard posed by this amount of excess carbon dioxide is questionable. As for SO_2, its projected concentration in the stack gas exceeds its MATE value by a factor of twenty, but it still meets the new source performance standard of 0.8 lb SO_2 per million Btu input.* Vanadium pentoxide, V_2O_5, and chromic oxide, Cr_2O_3, pose the greatest potential hazard based on the projected concentration/MATE ratios of Table 4-9, followed by SO_2, NiO, V_2O_4, VO, and elemental chromium and vanadium, and the borderline case of CO_2.

As previously stated, it is assumed for the case of this approximation that 90% of the trace species are accumulated in the limestone slurry. The slurry composition based on this assumption is shown in Table 4-10. The trace element concentration in micrograms per liter assumes a sludge density of 1.12×10^9 jg/l (sp.gr. = 1.12).[8] Again, the major potential hazards are posed by nickel, vanadium, chromium, and cobalt compounds (oxides and sulfates).

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* Based on FGD-limestone material balance:

$324.53 \text{ ppm} \times 5{,}100{,}000 \text{ lb/hr} = 1655 \text{ lb } SO_2 \text{ emitted/hr}$

$1655 \frac{\text{lb } SO_2}{\text{hr}} / 5166 \times 10^6 \frac{\text{Btu}}{\text{hr}} = .32 \text{ lb } SO_2\text{/million Btu}$

$0.32 \frac{\text{lb } SO_2}{\text{million Btu}}$ $0.8 \frac{\text{lb } SO_2}{\text{million Btu}}$ (current NSPS)

TABLE 4-9. PROJECTED COMPOSITION OF FGD STACK GAS(1)

	Fraction of Flue Gas (ppm)	Conc./MATE
V_2O_5	2.32	1876.5
Cr_2O_3	.13	102.5(2)
$SO_2(g)$	325	20.2
$CO_2(g)$	181,000	16.3
NiO	.28	15.3
V_2O_4	.005	4.26
VO	.004	3.08
Cr	.003	2.37
V	.003	2.06
CoO	.058	.946
$NiSO_4$	.008	.458(2)
CO(g)	18.0	.364
$Ni(OH)_2$	.005	.274(2)
Co_3O_4	.014	.224(2)
Al_2O_3	2.7	.221
SiO_2	2.0	.164
Ni	.003	.136
$CoSO_4$	.006	.096(2)
$N_2(g)$	731,000	N
$H_2O(g)$	60,000	N
$O_2(g)$	18,400	N
NO(g)	1,270	N

Notes: (1) All species in condensed phase unless otherwise noted.

(2) Based on MATE values estimated from others in same category.

TABLE 4-10. PROJECTED COMPOSITION OF FGD LIMESTONE SLUDGE

	Concentration in Sludge ug/l	MATE ug/l	Conc./MATE
$CaSO_4 \cdot 2H_2O$	1.4×10^8	--	--
$CaSO_3 \cdot 2H_2O$	1.9×10^8	--	--
$Ca(OH)_2$	5.05×10^7	--	--
$CaCO_3$	6.76×10^7	--	--
NiO	1.31×10^5	10	13,124
V_2O_5	1.07×10^6	150	7,157
$NiSO_4$	3937	10*	394
Cr_2O_3	5.85×10^4	250	234
$Ni(OH)_2$	2313	10*	231
Ni	1201	10	120
CoO	2.7×10^4	250	109
Co_3O_4	6362	250*	25.4
V_2O_4	2425	150	16.2
VO	1713	150	11.4
$CoSO_4$	2714	250*	10.9
Al_2O_3	1.27×10^6	1.5×10^5	8.45
V	1201	150	8.01
SiO_2	9.38×10^5	1.5×10^5	6.26
Cr	1312	250	5.25

* Based on MATE values estimated from others in same category.

The major factor which determines the actual environmental impact of the trace metals in the sludge is the propensity of the metals for being leached into the groundwater. If leaching could be held to zero, that is, no trace metal compounds escaping the sludge pond, then trace metal content of the sludge would be of little concern. Plastic sludge pond liners provide a means for eliminating the leaching problem, providing they do not split or break to allow seepage into the ground. Most installations, however, use the much cheaper clay-bottom pond, which does not totally prevent leaching. Chemical fixing of the sludge does not eliminate leaching, either, so that in most cases, the concentration and solubility of the sludge trace constituents must be considered in order to predict the potential environmental impact of sludge disposal.

Pollutant removal efficiencies for MgO slurry scrubbing are almost identical to those for limestone slurry scrubbing. Sulfur dioxide removal averages 90%, and condensed trace species removal via the venturi scrubber and the demister is also around 90%. Therefore, the stack gas composition from MgO FGD should be roughly equivalent to that of limestone FGD. Trace metal compounds retained by the slurry, however, are not deposited in a sludge pond, as in the case of non-regenerable slurry processes such as limestone scrubbing. Instead, the trace constituents must either exit the system via the SO_2 gas stream from the calciner or else build up in the magnesia slurry. Data on this area are incomplete, such that conclusions about the fate of trace compounds in the MgO system cannot be drawn at this point.

CAFB Emissions

There are three major effluent streams and one by-product stream from the CAFB process by which inlet stream pollutants can be emitted. Flue gas from the CAFB product gas boiler, spent stone from the limestone regenerator, and ash from the RESOX^{TM} unit are the major pollutant streams; and, sulfur from the sulfur condenser is a useful by-product.

A typical CAFB product gas composition is shown in Table 4-11. This product gas is the result of fluidized bed residuum combustion with limestone injection, which averages about 70% sulfur removal efficiency (SRE) judging by pilot plant data and can reduce the SO_2 emission rate to less than half of the

TABLE 4-11. CAFB FEEDSTOCK AND PRODUCT GAS ANALYSES(1)

Typical CAFB Feedstock Analysis(2)

Properties	Values
Specific Gravity	0.957
Kinematic Viscosity	
Cs at 140°F (60°C)	201
Cs at 210°F (99°C)	41.1
Carbon, percent by weight	85.9
Hydrogen, percent by weight	11.3
Sulfur, percent by weight	2.3
Nitrogen, percent by weight	0.35
Conradson Carbon, percent by weight	11.6
Asphaltene, percent by weight	7.1
Vanadium, ppm	366
Nickel, ppm	43
Sodium, ppm	36
Iron, ppm	3

CAFB Product Gas Composition

Component	Vol., Percent
Hydrogen	8.6 ± 3.0
Nitrogen	61 ± 5
Methane	6.4 ± 1.0
Carbon Monoxide	10 ± 3
Carbon Dioxide	9.5 ± 2.0
Ethylene	4.3 ± 0.6
Ethane	0.12 ± 0.04

Note: (1) Craig, J. W. T., et al., "Chemically Active Fluid-Bed Process for Sulphur Removal During Gasification of Heavy Fuel Oil - Third Phase," EPA-600/2-76-248, September, 1976.

(2) Amuay Atmospheric Residuum

EPA standard for SO_2. Nitrogen oxide production is also reduced. Pilot plant boiler combustion of CAFB gasifier product generates about 166 ppm NO_x vs. about 263 ppm for direct combustion of fuel oil.[34]

Initial mass balances performed by ERCA indicated near-complete retention of fuel and limestone trace elements on the gasifier bed. Those results, however, assumed homogeneous distribution of trace elements on the bed; but, further work by ERCA has indicated a preferential agglomeration of trace elements onto the finer particles in the bed, and volatization from the bed and condensation on the boiler cyclone fines.[12] Thus, it is expected that the boiler flue gas will be essentially free of trace metals; but, at this time, the distribution of trace metals between the spent stone and the cyclone fines is unknown. However, the current design for the Foster Wheeler $250MW_e$ plant calls for combination of the spent solids (bed stone and cyclone fines) in a storage silo and subsequent removal to a disposal site.[41] Thus, regardless of the distribution of trace elements between the spent stone and the fines, they will end up in the same place.

HDS Emissions

Typical HDS performance for three feedstocks is shown in Table 4-12. Desulfurization averages 96.5%, and demetallization ranges from 95% to 99% for the examples presented. Vanadium and nickel removal average 99% each for the low metal feedstocks considered. With higher metal content in the feed, catalyst poisoning becomes a problem.

The major effluent streams from the HDS process are separator off-gas, sulfur recovery unit acid gas (H_2S), and sour water from the sour water stripper, as well as the by-products naphtha and furnace oil. At this point, little is known about the distribution of trace pollutants between these streams.

A rough approximation for emissions from a boiler burning HDS-generated low sulfur fuel oil (LSFO) can be made by applying the demetallization factor of 95.3% to the products of combustion from a boiler without controls, shown in Table 4-7(a). The results, shown in Table 4-13, give a preliminary indication of potential problem pollutants. The SO_2 emission rate, based on 96.5% desulfurization, is seven times the SO_2 MATE value but still meets the New Source Performance Standard (NSPS) of 0.8 lb/million Btu.[11] Only seven trace metal compounds

TABLE 4-12. TYPICAL HDS PERFORMANCE (1)

	Kuwait Atmosphere Residua	No. 1 Light Arabian Atmospheric Residua	No. 2 Light Arabian Atmospheric Residua
Charge Stock Properties			
API Gravity	16.6	17.6	18.5
Sulfur, wt. %	3.8	3.0	2.93
Nitrogen, wt. %	.21	--	.16
Carbon Residue, Rams, Wt. %	8.3	--	6.79
Nickel, ppm	15.0	40 (Ni + V)	7.3
Vanadium, ppm	45.0		27.0
Yields: Run Avg.			
Desulfurization, %	97	96.7	95.9
API Gravity	26	23.2	25.1
Sulfur, wt. %	0.1	0.1	0.12
Nitrogen, wt. %	0.11	--	0.09
Carbon Residue, Rams, wt. %	2.2	--	2.28
Nickel, ppm	0.2	--	0.5
Vanadium, ppm	0.1	--	0.3
Demetallization, %	99.2	--	95.3
H_2S, wt. %	3.94	2.8	--
NH_3, wt. %	0.11	0.1	--
C_1-C_4, wt. %	1.4	1.15	--
C_5-375°F Naphtha, Vol. %	3.93	3.04	--
375°F + Fuel Oil, Vol. %	98.93	98.15	--
Chem. H_2 Consumption, SCF/bbl	860	660	--

Note: (1) from "Latest Data on Gulf HDS Process," Gulf Science and Technology Co., Hydrocarbon Processing, May 1977, pp. 97-104; and, "The Gulf HDS Process," Gulf Research and Development Co., August 16, 1974.

TABLE 4-13. PROJECTED HDS LSFO-FIRED BOILER COMBUSTION PRODUCTS

Combustion Product	Fraction of Flue Gas (ppm)	Conc./ MATE
SO_2	116.6	7.2
CO_2	185,000	16.7
CO	185.0	3.74
V_2O_5	1.12	906
Cr_2O_3	.061	49
NiO	.136	7.4
V_2O_4	.0025	2.1
VO	.0018	1.5
Cr	.0014	1.1
V	.0012	1.0
CoO	.028	.46
$NiSO_4$	.0041	.22
$Ni(OH)_2$	.0024	.13
Co_3O_4	.0067	.11
Al_2O_3	1.32	.11

are projected to exceed their MATE values. They are all either oxides or elemental forms of V, Ni, and Cr. Lack of adequate engineering information prevents a meaningful projection of the environmental impact of spent catalyst disposal at this point. Spent catalyst disposal is, however, a major environmental concern associated with HDS, due to the quantities of sulfur, carbon, and trace metals retained on the catalyst bed.

POX Emissions

The partial oxidation process generates a low-Btu, virtually carbon-free gas for use as a gas turbine feedstock. The major pollutant streams are flue gas and wastewater from the sulfur recovery process, wastewater from the carbon/gas separator, wastewater from the fuel preparation unit, and combustion products from the gas turbine. A typical analysis of gasifier product gas is shown in Table 4-14.

The water scrubber which follows the reactor removes essentially all water soluble contaminants in the product gas, as well as the carbon soot, which remains suspended in the water. The contaminants include: trace metals (mostly vanadium and nickel); hydrogen cyanide (HNC); ammonia (NH_3); and trace amounts of formic acid (HCO_2H). The suspended carbon soot is removed by naphtha extraction or other recovery methods and recycled to the gasifier. Some ash and trace metals are recycled with the carbon soot; but, most will remain in the wash water, which is subsequently treated for removal of hydrogen cyanide, ammonia, and formic acid. Some trace metals remain in the ash, which collects in the bottom of the gasifier. Operating experience indicates that perhaps 50% of vanadium, sodium, and nickel drop out with the ash; and, the rest of these and other trace metals are removed from the gas stream by the water scrubber. Following the water scrubber, the gas passes through a contactor containing a sorbent for removal of H_2S and minor sulfur compounds, such as carbonyl sulfide and carbon disulfide, so that the resultant low-Btu gas stream is virtually free of particulate matter and sulfur compounds.

The projected trace emissions of Table 4-15 for a boiler burning POX product gas are based on the residual oil combustion products of Table 4-7(a), assuming 99% removal of trace metals in the gasifier ash and product gas wash. Based on this approximation and the MATE values, the only compounds presenting a potential health or ecological hazard as air pollutants are vanadium pentoxide,

TABLE 4-14. TYPICAL POX PRODUCT GAS COMPOSITION FOR RESIDUAL OIL GASIFICATION WITH AIR(1)

Composition	Concentration (% Vol.)
CO_2	2.36
CO	22.29
H_2	16.66
CH_4	0.03
N_2	57.55
A	0.70
H_2S	0.39
COS	0.02
H_2O	--

(1) "The Shell Gasification Process," Shell Internationale Research Maatschappij N.V., The Hague, Holland, January, 1974.

TABLE 4-15. PROJECTED TRACE EMISSIONS FOR BOILER BURNING POX PRODUCT GAS

	Fraction of Flue Gas (ppm)	Conc./MATE (Air)
V_2O_5	.238	192.66
Cr_2O_3	.013	10.52*
NiO	.029	1.57
V_2O_4	.00054	.437
VO	.00039	.316
Cr	.00030	.243
V	.00026	.211
CoO	.00600	.0971
$NiSO_4$	.00087	.0470*
$Ni(OH)_2$	.00052	.0281*
Co_3O_4	.00142	.0230*
Al_2O_3	.281	.0227
SiO_2	.208	.0168
Ni	.00026	.0140
$CoSO_4$	.00061	.00988*

* Based on MATE values estimated from others in the same category.

chromic oxide, and nickel oxide. All other trace compounds have projected emission levels below their MATE values.

Assuming that 99% of the trace metal compounds are removed from the product gas stream and that roughly half of that reduction occurs as retention in gasifier ash, then about 50% of the input trace metals will exit the system as contaminants in the wash water. Based on that assumption and the residual oil combustion products, the estimated concentration of major trace pollutants in POX wastewater is as shown in Table 4-16. Comparison of projected pollutant levels with MATE values indicates that a potential environmental problem exists in the high levels of trace metal compounds in the wastewater.

4.1.2 Actual Baseline Emissions

This section covers the available chemical and physical properties of waste streams found in the commercial operations of FGD, POX, and HDS in Japan. The emissions analyses are based on grab samples taken in Japan in 1977. The spark source mass spectroscopic (SSMS) analyses were performed by Northrop Services, Inc., Research Triangle Park, North Carolina. Fugitive emissions and boiler wastewater blowdown streams were not considered because they are well defined by other EPA projects specifically addressed to these objectives.

A spark source mass spectrographic analysis is shown in Table 4-17 for the aluminum sulfate/limestone FGD process in Japan. The elements were retabulated in Table 4-18 for purposes of ranking the potentially hazardous pollutants by MATE ratio (Column 1), maximum pollutant concentration range in sludge (Column 2), and comparison with the current concentration goals of the MATE values (for land). Table 4-18 shows a total of 14 elements above ratio of one, indicating nickel at the top of the list of suspect toxic elements followed by selenium, zinc, cobalt, vanadium, and arsenic.

The trace element emissions from the residual fuel oil combustion emissions from a magnesia-limestone double alkali FGD system are shown in Table 4-19. The limit of detection for this sample is 0.8 mg/g on the elements not reported. Table 4-20 tabulates the magnesia-gypsum sludge potentially toxic pollutants in the order of high MATE ratios to low. In this process, the important pollutants to observe are selenium, nickel, vanadium, zinc, chromium, and cobalt.

Table 4-21 is a tabulation of the SSMS of trace elements discharge in a waste stream from the sodium sulfite/weak acid, regenerable FGD process in

TABLE 4-16. PROJECTED TRACE CONTAMINANTS IN POX WASTEWATER

Pollutant	lb/hr to Wastewater	Conc. in Wastewater (ug/l)	Conc./MATE
NiO	3.30	51400	5140
V_2O_5	27.11	422000	2813
$NiSO_4$	.099	1540	154*
Cr_2O_3	1.48	23000	92
$Ni(OH)_2$	.059	920	92*
Ni	.030	470	47
CoO	.683	10600	42.4
Co_3O_4	.162	2520	10.1*
V_2O_4	.062	970	6.5
VO	.044	690	4.6
$CoSO_4$	.069	1070	4.3*
Al_2O_3	32.01	498000	3.3
V	.030	470	3.1
SiO_2	23.69	369000	2.5
Cr	.034	530	2.1

* Based on MATE values estimated from others in the same category.

TABLE 4-17. SPARK SOURCE MASS SPECTROGRAPHIC ANALYSIS OF JAPANESE LIMESTONE FGD SLUDGE

Element	Concentration, in ug/g
Ba	120.
Sr	230.
Se	8.
As	1.5
Ge	2.6
Zn	190.
Ni	63.
Co	16.
Fe	610.
Mn	36.
V	110.
Ca	110,000.
K	200.
P	5.5
Si	540.
Al	640.
Mg	380.
Na	200.
Ash	74.1

Note: (1) Sample from aluminum sulfate-gypsum sludge Dowa Basic $(Al)_2(SO_4)_3$-Gypsum.

TABLE 4-18. FGD SLUDGE POLLUTANT RANKING

Element	MATE Ratio	Maximum Concentration in ug/g	Concentration Goal in ug/g (MATE-Values)
Ni	140.0	63.3	0.45
Se	80.0	<8.0	0.1
Mn	72.0	36.0	0.2
Zn	38.0	<190.0	5.0
Co	32.0	16.0	1.5
V	22.0	110.0	5.0
Ba	12.0	120.0	10.0
Al	4.0	640.0	4.0
K	3.30	200.0	60.0
Fe	3.05	610.0	200.0
As	3.00	1.5	3.0
Sr	2.50	230.0	92.0
Mg	2.24	380.0	170.0
P	0.18	5.5	30.0
Ge	0.15	2.6	5.0
Na	0.13	200.0	1600.0
Ca	--	110,000.0	480.0
Si	--	540.0	300.0

TABLE 4-19. SSMS ANALYSIS OF JAPANESE MAGNESIA-GYPSUM FGD SLUDGE

Element	Concentration, in ug/g
Ba	29.
Se	30.
Ga	7.7
Zn	300.
Cu	17.
Ni	45.
Co	48.
Fe	1,400.
Cr	24.
V	220.
Ti	69.
Ca	200,000.
K	510.
Cl	88.
P	50.
Si	1,300.
Al	27.
Mg	770.
Na	100.
Ash	78.

TABLE 4-20. MAGNESIA-GYPSUM FGD SLUDGE POLLUTANT RANKING

Element	MATE Ratio	Maximum Concentration in ug/g	Concentration Goal in ug/g (MATE-Values)
Se	300.0	< 30.0	0.1
Ni	100.0	< 45.0	0.45
Zn	60.0	<300.0	5.0
Cr	48.0	24.0	0.5
V	44.0	220.0	5.0
Co	32.0	48.0	1.5
Cu	17.0	17.0	1.0
K	8.5	510.0	6
Fe	7.0	1,400.0	200.0
Mg	4.5	770.0	170.0
Si	4.3	1,300.0	300.0
Ba	2.9	29.0	10.0
P	1.7	50.0	30.0
Ti	0.38	69.0	180.0
Al	0.17	27.0	160.0
Na	0.06	100.0	1,600.0
Ga	0.05	7.7	150.0
Cl	0.034	88.0	2,600.0
Ca	--	200,000.0	480.0

TABLE 4-21. SSMS ANALYSIS OF JAPANESE SODIUM SULFITE/WEAK ACID, FGD SLUDGE

Element	Concentration, in ug/g
Pr	.52
Ce	2.4
La	1.6
Ba	97.
Zr	16.
Sr	160.
Zn	42.
Cu	25.
Ni	40.
Co	17.
Fe	14,000.
Mn	450.
Cr	1,400.
V	500.
Ti	230.
Sc	9.5
Ca	8,900.
K	13,000.
Cl	42.
P	200.
Si	Major
Al	11,000.
Mg	5,100.
Na	16,000.
Ash	56.5

Japan. The approximate detection limit for elements not reported is 0.06 ug/g. Table 4-22 shows the pollutant inventory of the sodium sulfite/weak acid FGD system with very high concentrations and MATE ratios for chromium, manganese, vanadium, nickel, cobalt, zinc, and strontium.

Table 4-23 is a spark source mass spectrographic analysis of carbon recovery effluent from a partial oxidation process burning residual oil. The limit of detection for the elements not reported is 0.01 ug/g. The bulk of (¼") spherical, soft, and black soot pellets were ashed to a trace residue of less than 1 percent. Thus, most of this material is unburnt carbon with very small concentrations of the total trace elements.

Table 4-24 indicates very high MATE ratios of nickel and vanadium, which are typical of residual oil from Arabian crude oils. Most of the bulk quantities of trace elements are in the wastewater effluent stream from the POX gasifier discharge quench vessel and the water wash tower.

4.2 TEST PROGRAM DEVELOPMENT

The residual oil facilities are complex, multiwaste stream generating systems. To carry out environmental assessment measurement programs in a manner suitable to the needs of EPA for the sampling and analysis tasks, one must be familiar not only with the Level 1 and Level 2 sampling and analysis requirements but also with the details of the processes themselves. To facilitate cost-effectiveness, the specific programs designed for each facility must include, in addition to Level 1 measurements, limited Level 2 type field measurements for specific pollutants identified through engineering calculations. Although engineering studies and identification of specific pollutants (for example, SO_2, H_2S, $Ni(CO)_4$, V_2O_5, and NO_x) are of concern, the sampling and analysis should provide input to these decisions and integrate them smoothly into the basic Level 1 sampling program. Several residual oil processes are to be sampled in this program, and specific pollutant concentrations from various waste streams will be estimated beforehand.

In addition to considerations involving plant design and operating conditions, a detailed sampling plan must include logistical considerations such as power, laboratory space and facilities, water, ports, and scaffolding available on site. Shipment of sampling equipment and chemicals to a site must be

TABLE 4-22. SODIUM SULFITE/WEAK ACID FGD SLUDGE ANALYSIS POLLUTANT RANKING

Element	MATE Ratio	Maximum Concentration in ug/g	Concentration Goal in ug/g (MATE-Values)
Cr*	2,800.0	< 1,400.0	0.5
Mn*	900.0	450.0	0.5
V	100.0	500.0	5.0
Ni	88.9	< 40.0	0.45
Al*	68.8	11,000.0	160.0
Fe*	70.0	14,000.0	200.0
Mg	30.0	5,100.0	170.0
Cu*	25.0	25.0	1.0
Co	11.3	17.0	1.5
Ba	9.7	97.0	10.0
Zn	8.4	42.0	5.0
Sr	1.74	160.0	92.0
Ti	1.28	230.0	180.0
Zr	0.94	16.0	15.0
Cl	0.16	42.0	2,600.0
Si	--	Major	
Na	--	16,000.0	1,600.0
K	--	13,000.0	60.0
Ca	--	8,900.0	480.0
Ce	2.0	2.4	1,100.0
La	0.00050	1.6	3,400.0
Pr	0.00004	0.52	1,500.0
P	.0059	200.0	30.0
Se		9.5	1,610.0

* These elements may be erroneously high in concentration as a result of corrosive action on the scrubber materials of construction.

TABLE 4-23. SSMS ANALYSIS OF JAPANESE POX CARBON PELLETED RESIDUE

Element	Concentration in ug/g
Pb	.12
Ba	1.2
Mo	2.6
Zr	.04
Sr	1.2
Ga	.97
Ni	480.
Co	2.6
Fe	480.
Mn	3.6
Cr	8.5
V	540.
Ti	2.3
Sc	.32
Ca	340.
K	200.
Cl	3.0
P	15.
Si	980.
Al	88.
Mg	77.
Na	240.
Ash	1.

TABLE 4-24. PARTIAL OXIDATION CARBON RESIDUE POLLUTANT RANKING

Element	MATE Ratio	Maximum Concentration in ug/g	Concentration Goal in ug/g (MATE-Values)
Ni	24,000.0	480.0	0.02
V	1,800.0	540.0	0.3
Al	44.0	88.0	2.0
Cr	29.8	8.5	0.286
Mn	18.0	3.6	0.2
Co	5.2	2.6	0.5
K	3.33	200.0	60.0
Ti	1.4	2.3	1.6
Pb	1.2	0.12	0.10
Ba	0.545	1.2	2.20
Mo	0.186	2.6	14.0
Ga	--	0.97	14.9
Sr	0.0130	1.2	92.0
Zr	0.0027	0.04	15.0
Sc	0.0020	0.32	1,600.0
Cl	0.0012	3.0	2,600.0
Si	3.3	980.0	300.0
Fe	2.4	480.0	200.0
Mg	2.1	77.0	36.6
Ca	0.71	340.0	480.0
P	0.5	15.0	30.0
Na	0.15	240.0	1,600.0

Note: (1) Sample from gasifier discharge of carbon recovery pellets with trace metals acid from residual oil.

arranged well in advance, particularly when sampling in a foreign country.

The goal of the sampling operation is to complete the Level 1 and 2 requirements in one trip. This is especially true in the case of the Japanese sites for which a follow-up sampling visit would be extremely expensive. Our approach to this program would combine a complete Level 1 (SASS, GC, liquid, solid streams) test with collection of duplicate samples plus special Level 2 tests for those pollutants identified in the engineering assessment.

The laboratory analysis phase of the program is more flexible than the sampling portion in that decisions to conduct additional Level 2 analyses often can be made without resampling after Level 1 analyses are completed. To ensure that sufficient sample quantities will be available for Level 2 analyses, additional (to Level 1) liquid and solid waste samples will be taken at each facility and duplicate SASS runs will be made when feasible. The overall analytical plan will cover Level 1, those additional pollutants identified as a priority by the engineering estimates, and those potential pollutants uncovered by Level 1.

4.2.1 Sampling and Analysis Matrix

Completion of the environmental data acquisition requires characterization of the input/output streams for each process under study.[30] Thus, the sampling and analysis program to obtain the data necessary for stream characterization is an important element in the environmental assessment effort.[31]

A phased approach to environmental assessment sampling and analysis has been developed by the EPA, and Catalytic's intention is to follow the established methodology. Level 1 techniques will be employed, but simplifying Level 1 assumptions will not be allowed to restrict data gathering when very little additional time and effort will result in substantial additional data collection.[40]

A sampling/analysis program has been developed which conforms to EPA Level 1 guidelines. A sampling/analysis matrix, developed as a tool to aid in carrying out the sampling/analysis program, has been developed and is presented for the purpose of illustrating, clearly and concisely, the logical procedure being followed to develop the required stream characterization data.

A sampling/analysis matrix is presented for a residual oil-fired utility boiler without controls, as well as for each of the major utilization processes being considered: hydrodesulfurization, regenerable flue gas desulfurization (MgO scrubbing), non-regenerable flue gas desulfurization (limestone scrubbing), partial oxidation, and the chemically active fluid bed process. An example of the use of the sampling/analysis matrix is given in the interest of clarity.

The sampling program for environmental assessment must be much more extensive than those programs conducted for process or control data collection, since the total pollution potential of all process waste streams must be identified. All waste streams must be sampled, and all substances of potential environmental insult must be detectable above a minimal level of concern.[16]

The phased approach to environmental assessment involves sampling and analysis on three levels. Level 1 sampling/analysis is designed for an accuracy factor of ± 3 (-33% to 300% of the true value), and the resultant data is used for pollutant stream prioritization. Level 2 involves detailed sampling and analysis, applied first to those streams of highest priority, as defined by Level 1; and, Level 3 involves continuous monitoring of indicator substances for evaluation of long-term process variation.

A generalized sampling matrix for gas, liquid, and solid streams is shown in Table 4-25. The generalized Level 1 physical, chemical, and biological analysis scheme is shown in Figure 4-2. Design of a Level 1 sampling/analysis matrix involves answering four basic questions: (1) Where in the system are the samples to be taken? (2) How are the samples to be taken? (3) What are the potential pollutants or pollutant categories in each stream? and (4) What method of analysis is used to determine the level of each potential pollutant in each stream?

The answers to the first two questions are given in Figures 4-3 through 4-8. The numbered streams on the flow diagrams indicate where in the system the samples are to be taken, and the accompanying tables indicate the stream conditions and the techniques to be used in obtaining the desired samples.

The third and fourth questions are answered by Tables 4-26 through 4-31, which list the potential pollutants in each stream, along with the methods

TABLE 4-25. LEVEL 1 SAMPLING*

Stream	Sample Size	Location	Sampling Procedure
Gas	30 m^3	Ducts, stacks	SASS train
Liquid	10 liter	Lines or tanks	Tap or valve sampling
		Open free-flowing streams	Dipper method
Solids	1 kg	Storage piles	Coring
		Conveyors	Full stream cut

* Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1, EPA-600/2-77-115 (NTIS No. PB 268563/AS), June 1977.

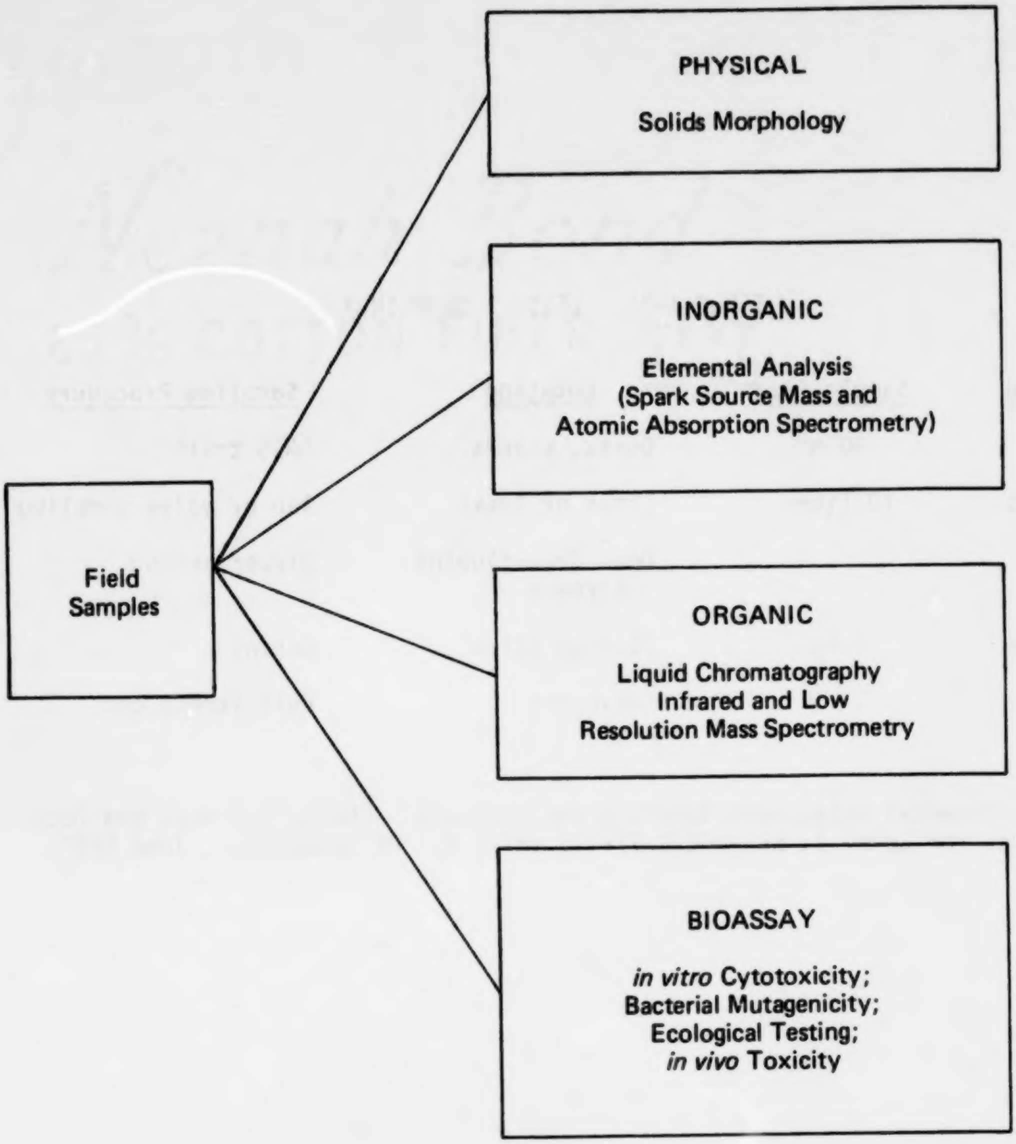
Field Samples
PHYSICAL
Solids Morphology
INORGANIC
Elemental Analysis (Spark Source Mass and Atomic Absorption Spectrometry)
ORGANIC
Liquid Chromatography Infrared and Low Resolution Mass Spectrometry
BIOASSAY
in vitro Cytotoxicity; Bacterial Mutagenicity; Ecological Testing; *in vivo* Toxicity

Figure 4-2 - Level 1 Analysis*

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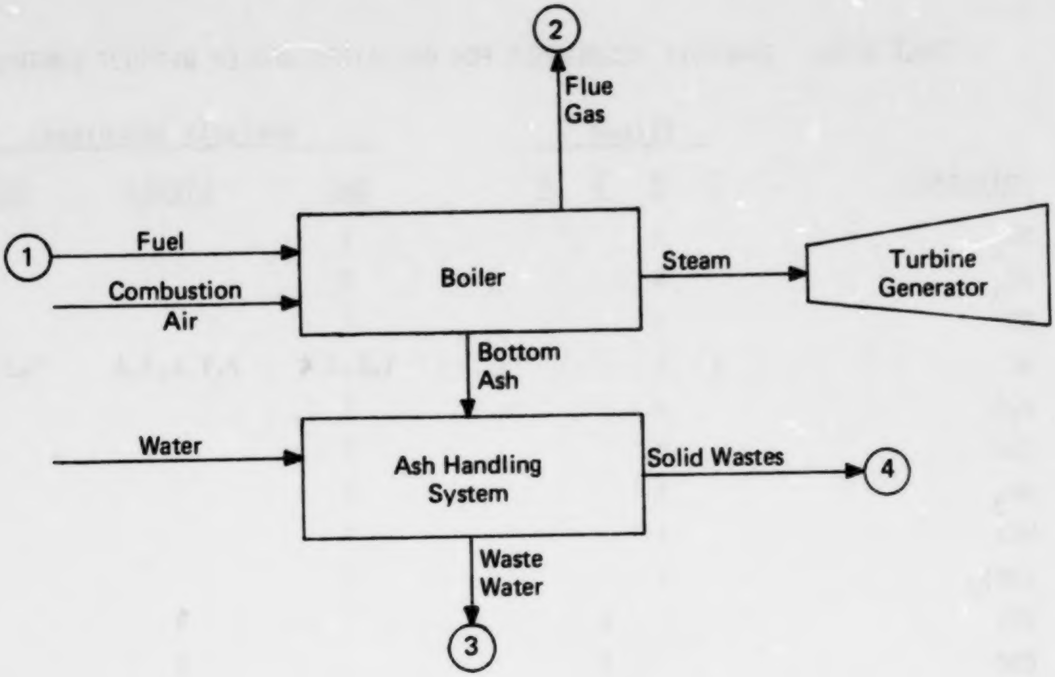
*Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1, EPA-600/2-77-115 (NTIS No. PB 268563/AS), June 1977.



Stream	Description	Conditions			Sampling Method
		Temp.	Pressure	Phase	
1	Residual Oil Feed	Ambient	Atmospheric	1	Grab
2	Stack Gas	400°F	Atmospheric	g	SASS[1]
3	Wastewater from Ash Handling	200°F	Atmospheric	1	Grab[2]
4	Bottom Ash	200°F	Atmospheric	s	Grab[2]

Notes:

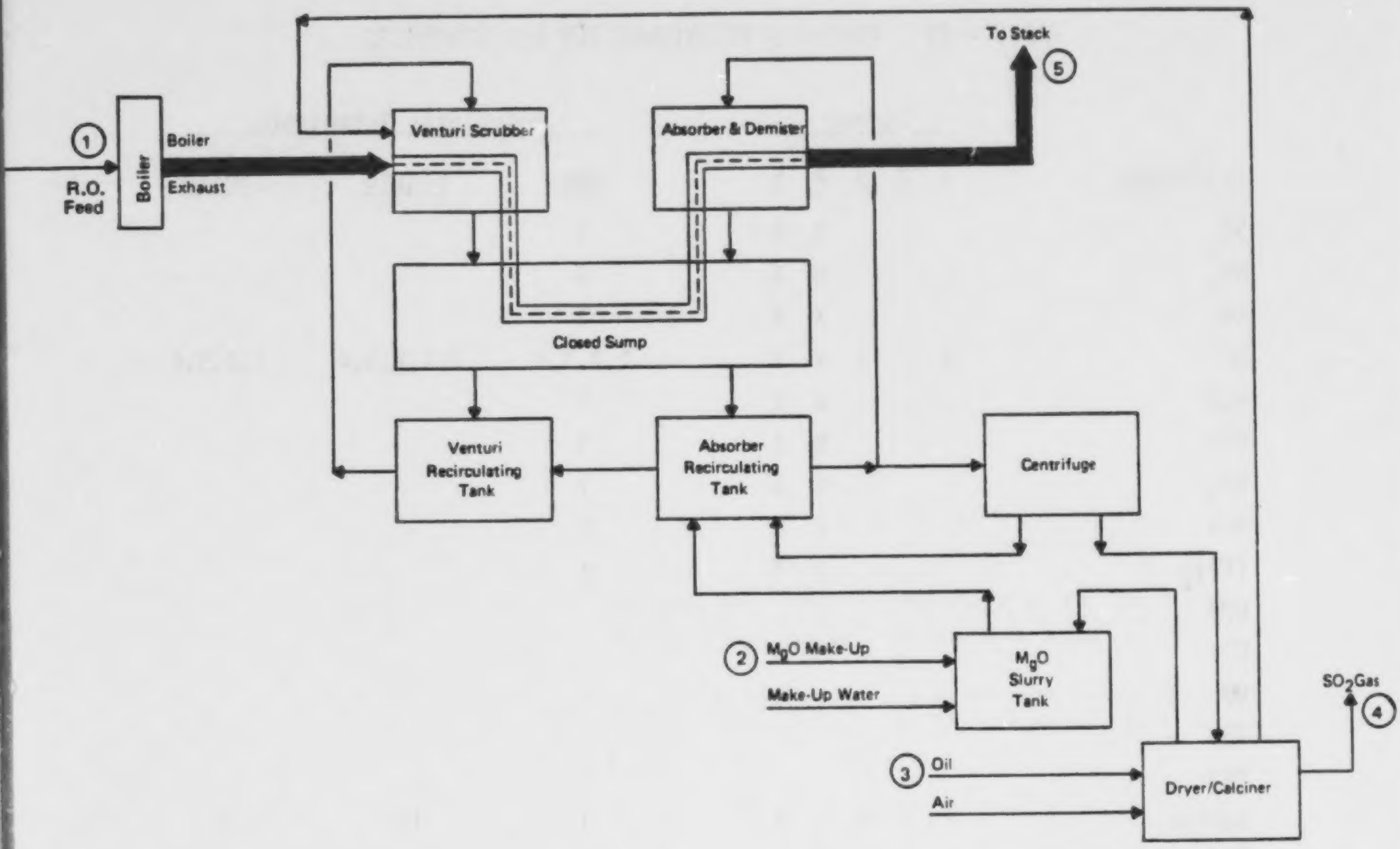
1. Additional methods may include EPA Method 5 for inorganics, and the Controlled Condensation Train for SO_x.
2. To be taken between ash handling system emission point and final disposal point. Time-composite may be desirable to account for process conditions which vary with time.

Figure 4-3 - Sampling Matrix for Oil-Fired Boiler without Controls

TABLE 4-26. ANALYSIS TECHNIQUES FOR OIL-FIRED BOILER WITHOUT CONTROLS

	Stream				Analysis Techniques		
Pollutant	1	2	3	4	Gas	Liquid	Solid
SO_x		X			1		
NO_x		X			8		
CO		X			1		
HC	X	X			1,2,3,4	7,1,2,3,4	1,2,3,4
H_2S		X			1		
COS		X			1		
NH_3		X			1		
HCN		X			1		
$(CN)_2$		X			1		
BOD			X			9	
COD			X			9	
DO			X			9	
TDS			X			9	
TSS			X			9	
Sulfur	X					5	
Nitrogen	X					13	
Carbon	X	X		X	5	5	5
Hg, As, Sb	X	X	X	X	6	6	6
Cl, F	X	X	X	X	10	10	10
Other Trace Metals	X	X	X	X	5	5	5
Ash/Particulate	X	X		X	5	5	5
Sulfates			X			11	
Nitrates			X			12	

1. Gas Chromatography (GC)
2. Liquid Chromatography (LC)
3. Infrared Spectrometry (IR)
4. Low Resolution Mass Spectrometry (LRMS)
5. Spark Source Mass Spectrometry (SSMS)
6. Atomic Absorption (AA)
7. CH_2Cl_2 Extraction
8. Chemiluminescence
9. Hach or Bausch and Lomb reagent test kits
10. Wet Chemical Analysis Techniques
11. Turbidimetric method for sulfates
12. Brucine-nitrate procedure
13. Combustion Titrimetric/Spectometric method



Stream	Description	Conditions			Sampling Method
		Temp.	Pressure	Phase	
1	Residual Oil Feed	Ambient	Atmospheric	l	Grab
2	MgO Make-Up	Ambient	Atmospheric	s	Grab
3	Oil to Dryer/Calciner	Ambient	Atmospheric	l	Grab
4	Calciner Off-Gas (SO_2)	100°F	Atmospheric	g	SASS[1]
5	Cleaned Stack Gas	300°F	Atmospheric	g	SASS[1]

Notes:

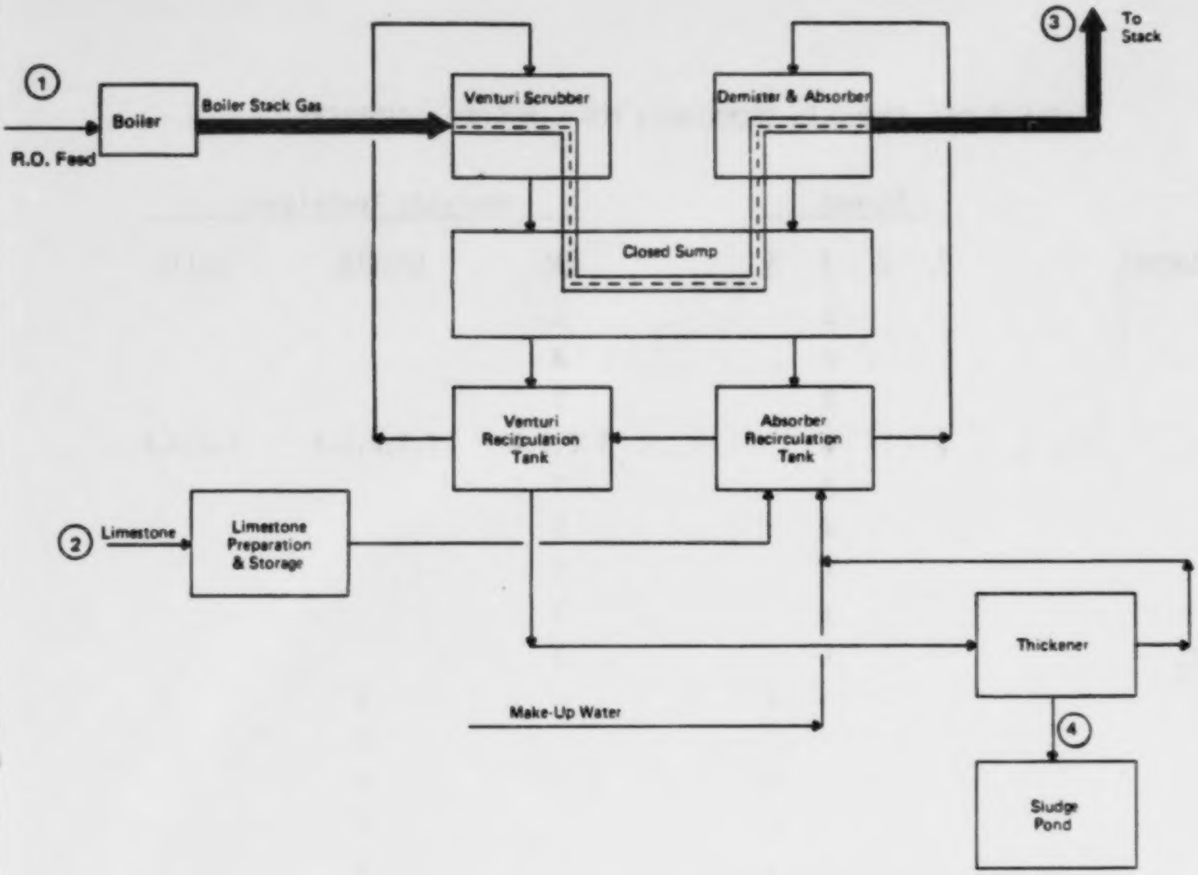
1. Additional methods may include EPA Method 5 for inorganics and the Controlled Condensation Train for SO_x.

Figure 4-4 - Sampling Matrix for MgO Scrubbers

TABLE 4-27. ANALYSIS TECHNIQUES FOR MgO SCRUBBERS

	Stream					Analysis Techniques		
Pollutant	1	2	3	4	5	Gas	Liquid	Solid
SO_x				X	X	1		
NO_x				X	X	8		
CO				X	X	1		
HC	X		X	X	X	1,2,3,4	7,1,2,3,4	1,2,3,4
H_2S				X	X	1		
COS				X	X	1		
NH_3				X	X	1		
HCN				X	X	1		
$(CN)_2$				X	X	1		
BOD								
COD								
DO								
TDS								
TSS								
Sulfur	X	X	X	X	X	1	13	5
Nitrogen	X		X	X	X	5	5	
Carbon	X		X	X	X	5	5	
Hg, As, Sb	X	X	X	X	X	6	6	6
Cl, F	X	X	X	X	X	10	10	10
Other Trace Metals	X	X	X	X	X	5	5	5
Ash/Particulate	X	X	X	X	X	5	5	5
Sulfates								
Nitrates								

1. Gas Chromatography (GC)
2. Liquid Chromatography (LC)
3. Infrared Spectrometry (IR)
4. Low Resolution Mass Spectrometry (LRMS)
5. Spark Source Mass Spectroscopy (SSMS)
6. Atomic Absorption (AA)
7. CH_2Cl_2 Extraction
8. Chemiluminescence
9. Hach or Bausch and Lomb reagent test kits
10. Wet Chemical Analysis Techniques
11. Turbidimetric method for sulfates
12. Brucine-nitrate procedure
13. Combustion Titrimetric/Spectometric method



Stream	Description	Conditions			Sampling Method
		Temp.	Pressure	Phase	
1	Residual Oil Feed	Ambient	Atmospheric	1	Grab
2	Limestone Feed	Ambient	Atmospheric	s	Grab
3	Cleaned Stack Gas	300°F	Atmospheric	g	SASS[1]
4	Sludge to Disposal Pond	200°F	Atmospheric	1	Grab[2]

Notes:

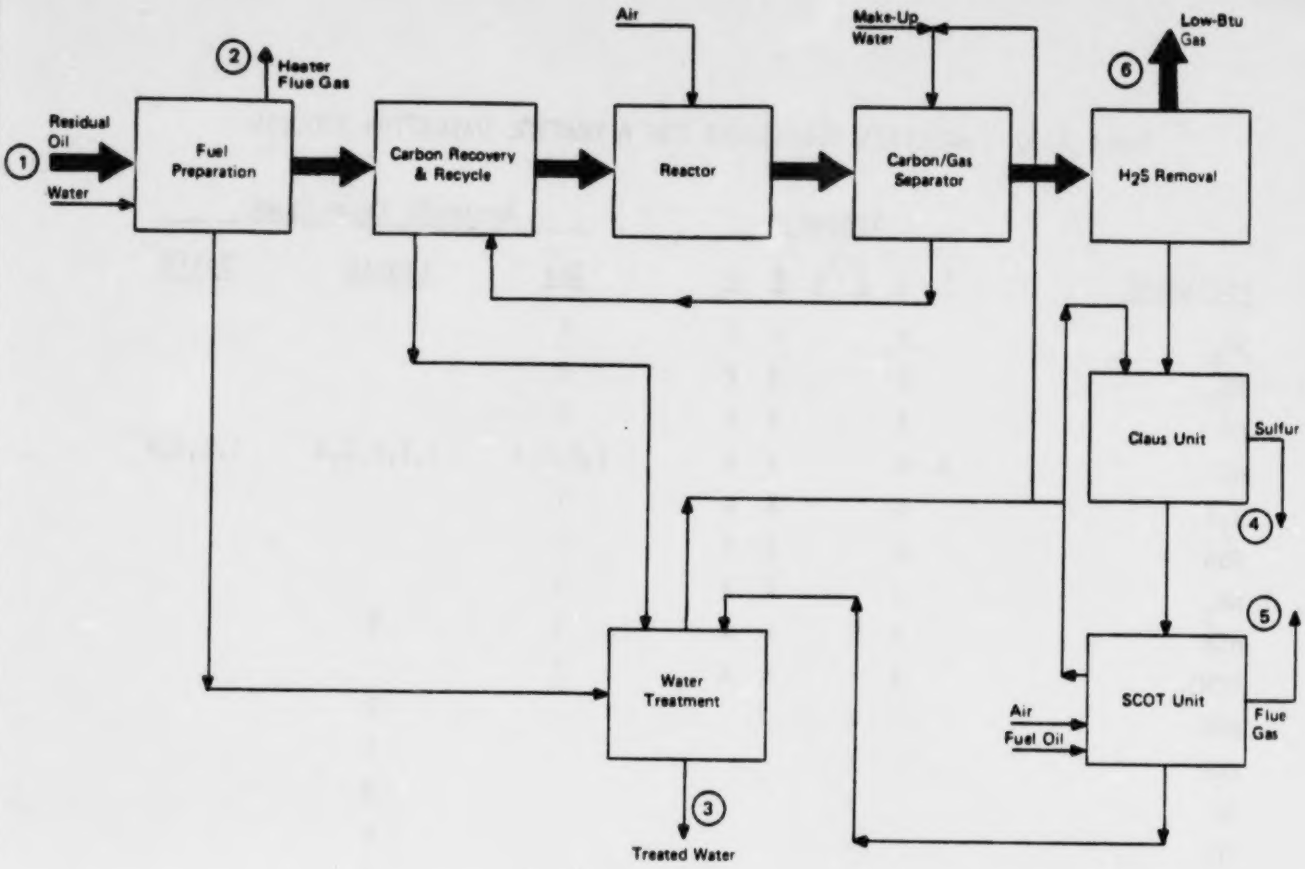
1. Additional methods may include EPA Method 5 for inorganics and the Controlled Condensation Train for SO_x.
2. To be taken between sludge thickener and disposal pond. Time-composite may be desirable to account for process conditions which vary with time.

Figure 4-5 - Sampling Matrix for Limestone Scrubbers

TABLE 4-28. ANALYSIS TECHNIQUES FOR LIMESTONE SCRUBBERS

	Stream				Analysis Techniques		
Pollutant	1	2	3	4	Gas	Liquid	Solid
SO_x			X		1		
NO_x			X		8		
CO			X		1		
HC	X		X		1,2,3,4	7,1,2,3,4	1,2,3,4
H_2S			X		1		
COS			X		1		
NH_3			X		1		
HCN			X		1		
$(CN)_2$			X		1		
BOD				X		9	
COD				X		9	
DO				X		9	
TDS				X		9	
TSS				X		9	
Sulfur	X					5	
Nitrogen	X					13	
Carbon	X	X	X	X	5	5	5
Hg, As, Sb	X	X	X	X	6	6	6
Cl, F	X	X	X	X	10	10	10
Other Trace Metals	X	X	X	X	5	5	5
Ash/Particulate	X		X	X	5	5	5
Sulfates				X		11	
Nitrates				X		12	

1. Gas Chromatography (GC)
2. Liquid Chromatography (LC)
3. Infrared Spectrometry (IR)
4. Low Resolution Mass Spectrometry (LRMS)
5. Spark Source Mass Spectroscopy (SSMS)
6. Atomic Absorption (AA)
7. Ch_2Cl_2 Extraction
8. Chemiluminescence
9. Hach or Bausch and Lomb reagent test kits
10. Wet Chemical Analysis Techniques
11. Turbidimetric method for sulfates
12. Brucine-nitrate procedure
13. Combustion Titrimetric/Spectometric method



Stream	Description	Conditions			Sampling Method
		Temp.	Pressure	Phase	
1	Residual Oil Feed	Ambient	Atmospheric	l	Grab
2	Heater Flue Gas	500°F	Atmospheric	g	SASS[1]
3	Wastewater	500°F	Atmospheric	l	Grab[2]
4	Sulfur from Sulfur Recovery Unit	500°F	Atmospheric	l	Grab[2]
5	Flue Gas from Sulfur Recovery Off-Gas Treatment	500°F	Atmospheric	g	SASS[1]
6	Low-Btu Product Gas	1000°F	275 psia	g	SASS[1]

Notes:

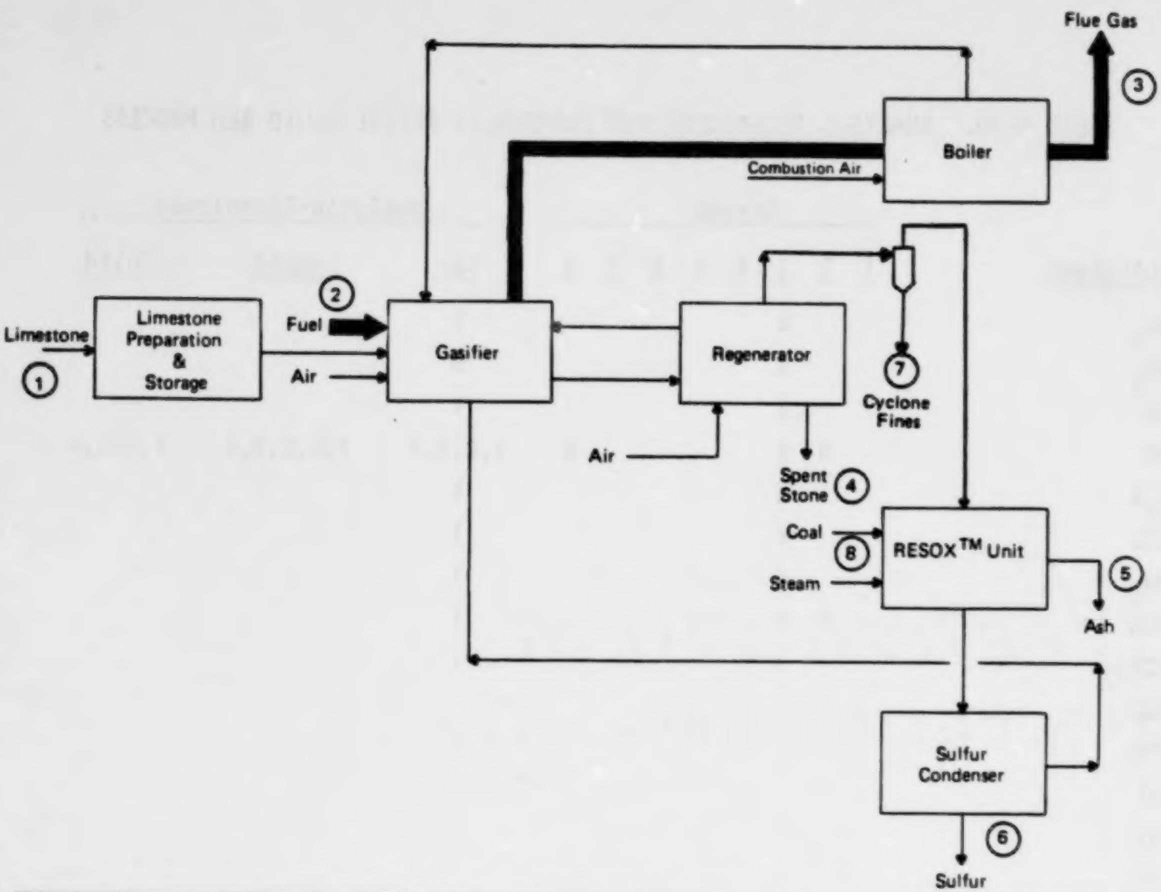
1. Additional methods may include EPA Method 5 for inorganics and the Controlled Condensation Train for SO_x.
2. Time-composite may be desirable to account for process conditions which vary with time.

Figure 4-6 - Sampling Matrix for Partial Oxidation Process

TABLE 4-29. ANALYSIS TECHNIQUES FOR A PARTIAL OXIDATION PROCESS

	Stream						Analysis Techniques		
Pollutant	1	2	3	4	5	6	Gas	Liquid	Solid
SO_x		X			X	X	1		
NO_x		X			X	X	8		
CO		X			X	X	1		
HC	X	X			X	X	1,2,3,4	7,1,2,3,4	1,2,3,4
H_2S		X			X	X	1		
COS		X			X	X	1		
NH_3		X			X	X	1		
HCN		X	X		X	X	1	5	
$(CN)_2$		X			X	X	1		
BOD			X					9	
COD			X					9	
DO			X					9	
TDS			X					9	
TSS			X					9	
Sulfur	X			X				5	5
Nitrogen	X							13	
Carbon	X	X	X	X	X	X	5	5	5
Hg, As, Sb	X	X	X	X	X	X	6	6	6
Cl, F	X	X	X	X	X	X	10	10	10
Other Trace Metals	X	X	X	X	X	X	5	5	5
Ash/Particulate	X	X	X	X	X	X	5	5	5
Sulfates			X					11	
Nitrates			X					12	

1. Gas Chromatography (GC)
2. Liquid Chromatography (LC)
3. Infrared Spectrometry (IR)
4. Low Resolution Mass Spectrometry (LRMS)
5. Spark Source Mass Spectroscopy (SSMS)
6. Atomic Absorption (AA)
7. CH_2Cl_2 Extraction
8. Chemiluminescence
9. Hach or Bausch and Lomb reagent test kits
10. Wet Chemical Analysis Techniques
11. Turbidimetric method for sulfates
12. Brucine-nitrate procedure
13. Combustion Titrimetric/Spectometric method



Stream	Description	Conditions			Sampling Method
		Temp.	Pressure	Phase	
1	Limestone Feed	Ambient	Atmospheric	s	Grab
2	Residual Oil Feed	Ambient	Atmospheric	l	Grab
3	Boiler Flue Gas	500°F	Atmospheric	g	SASS[1]
4	Spent Stone from Regenerator	450°F (after cooling)	Atmospheric	s	Grab[2]
5	Ash from Sulfur Recovery Unit	1400°F	Atmospheric	s	Grab[3]
6	Sulfur from Condenser	500°F	Atmospheric	l	Grab[3]
7	Regenerator Cyclone Fines	450°F (after cooling)	Atmospheric	s	Grab
8	Coal Feed to Sulfur Recovery Unit	Ambient	Atmospheric	s	Grab

Notes:

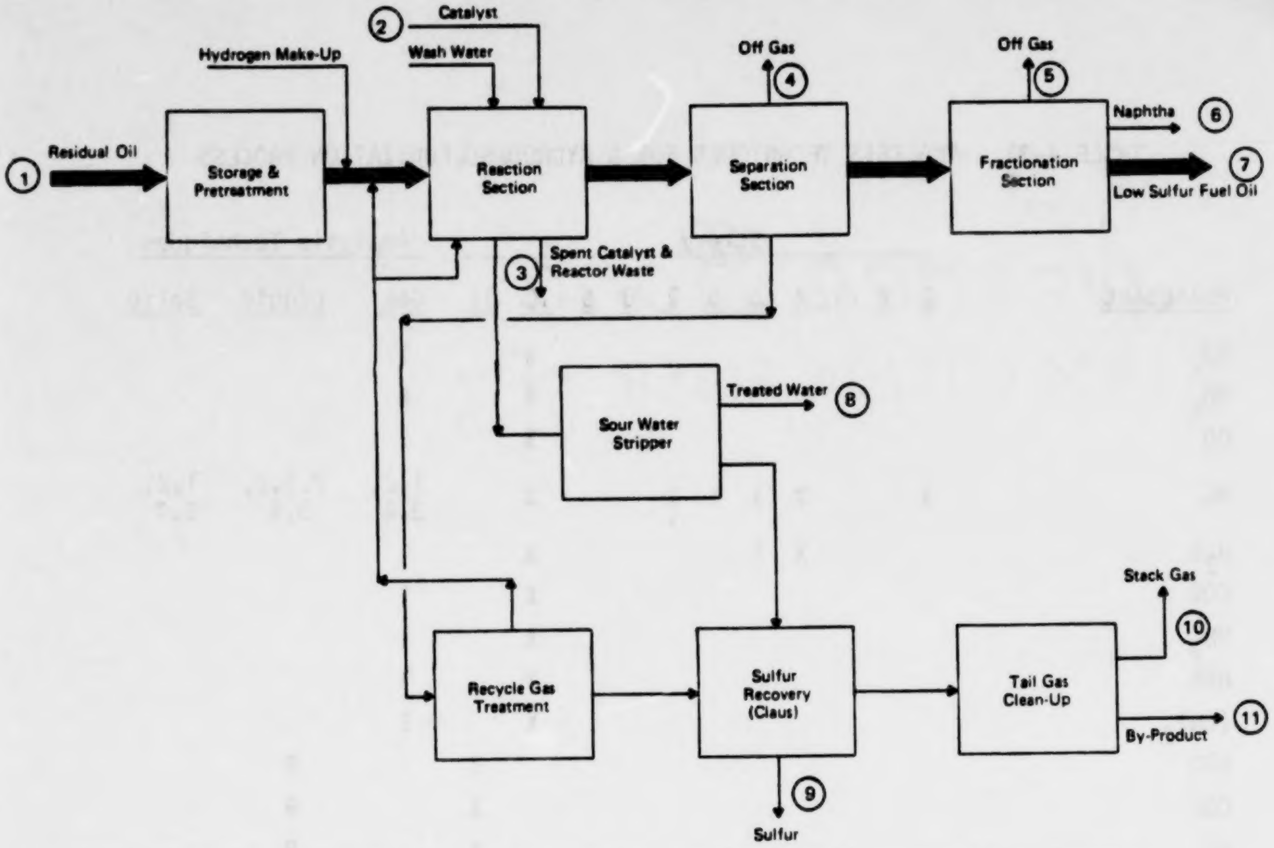
1. Additional methods may include EPA Method 5 for inorganics and the Controlled Condensation Train for SO_x.
2. Sample to be taken as close as possible to gasifier outlet. Time-composite may be desirable to account for process conditions which vary with time.
3. Time-composite may be desirable to account for process conditions which vary with time.

Figure 4-7 · Sampling Matrix for CAFB Process

TABLE 4-30. ANALYSIS TECHNIQUES FOR CHEMICALLY ACTIVE FLUID BED PROCESS

Pollutant	Stream 1	2	3	4	5	6	7	8	Analysis Techniques Gas	Liquid	Solid
SO_x			X						1		
NO_x			X						8		
CO			X						1		
HC		X	X					X	1,2,3,4	7,1,2,3,4	1,2,3,4
H_2S			X						1		
COS			X						1		
NH_3			X						1		
HCN			X						1		
$(CN)_2$			X						1		
BOD											
COD											
DO											
TDS											
TSS											
Sulfur		X		X	X	X	X	X		5	5
Nitrogen		X						X		13	13
Carbon	X	X	X	X			X	X	5	5	5
Hg, As, Sb	X	X	X	X	X	X	X	X	6	6	6
Cl, F	X	X	X	X	X	X	X	X	10	10	10
Other Trace Metals	X	X	X	X	X	X	X	X	5	5	5
Ash/Particulate		X	X	X	X	X	X	X	5	5	5
Sulfates				X							5
Nitrates											

1. Gas Chromatography (GC)
2. Liquid Chromatography (LC)
3. Infrared Spectrometry (IR)
4. Low Resolution Mass Spectrometry (LSMS)
5. Spark Source Mass Spectroscopy (SSMS)
6. Atomic Absorption (AA)
7. CH_2Cl_2 Extraction
8. Chemiluminescence
9. Hach or Bausch and Lomb reagent test kits
10. Wet Chemical Analysis Techniques
11. Turbidimetric method for sulfates
12. Brucine-nitrate procedure
13. Combustion Titrimetric/ Spectometric method



Stream	Description	Conditions			Sampling Method
		Temp.	Pressure	Phase	
1	Residual Oil Feed	Ambient	Atmospheric	l	Grab
2	Catalyst	Ambient	Atmospheric	s	Grab
3	Spent Catalyst and Reactor Waste	Ambient	Atmospheric	s	Grab[1]
4	Separator Off-Gas	300°F	180 psia	g	SASS[2]
5	Fractionator Off-Gas	300°F	40 psia	g	SASS[2]
6	Naphtha	300°F	40 psia	l	Grab
7	Low Sulfur Fuel Oil	200°F	40 psia	l	Grab
8	Treated Water From Stripper	200°F	Atmospheric	l	Grab[3]
9	Sulfur from Sulfur Recovery Unit	200°F	Atmospheric	l	Grab[3]
10	Stack Gas from Tail Gas Cleanup (H_2S)	500°F	Atmospheric	g	SASS[2]
11	By-product (water from Tail Gas Cleanup	300°F	Atmospheric	l	Grab[3]
		200°F	Atmospheric	l	Grab[3]

Notes:

1. Taken at end of run or during operation via purge tap if available.
2. Additional methods may include EPA Method 5 for inorganics and the Controlled Condensation Train for SO_x.
3. Time-composite may be desirable to account for process conditions which vary with time.

Figure 4-8 - Sampling Matrix for an HDS Process

TABLE 4-31. ANALYSIS TECHNIQUES FOR A HYDRODESULFURIZATION PROCESS

	Stream											Analysis Techniques		
Pollutant	1	2	3	4	5	6	7	8	9	10	11	Gas	Liquid	Solid
SO_x										X		1		
NO_x										X		8		
CO										X		1		
HC	X			X	X	X	X			X		1,2, 3,4	7,1,2, 3,4	1,2, 3,4
H_2S				X	X					X		1		
COS										X		1		
NH_3										X		1		
HCN										X		1		
$(CN)_2$										X		1		
BOD											X		9	
COD											X		9	
DO											X		9	
TDS											X		9	
TSS											X		9	
Sulfur	X		X			X	X	X	X				5	5
Nitrogen	X					X	X	X					13	13
Carbon	X		X			X	X	X	X		X		5	5
Hg, As, Sb	X		X	X	X	X	X	X	X	X	X	6	6	6
Cl, F	X		X	X	X	X	X	X	X	X	X	10	10	10
Other Trace Metals	X	X	X	X	X	X	X	X	X	X	X	5	5	5
Ash/Particulate	X		X			X	X	X	X	X	X	5	5	5
Sulfates			X					X	X		X		11	5
Nitrates			X					X			X		12	5

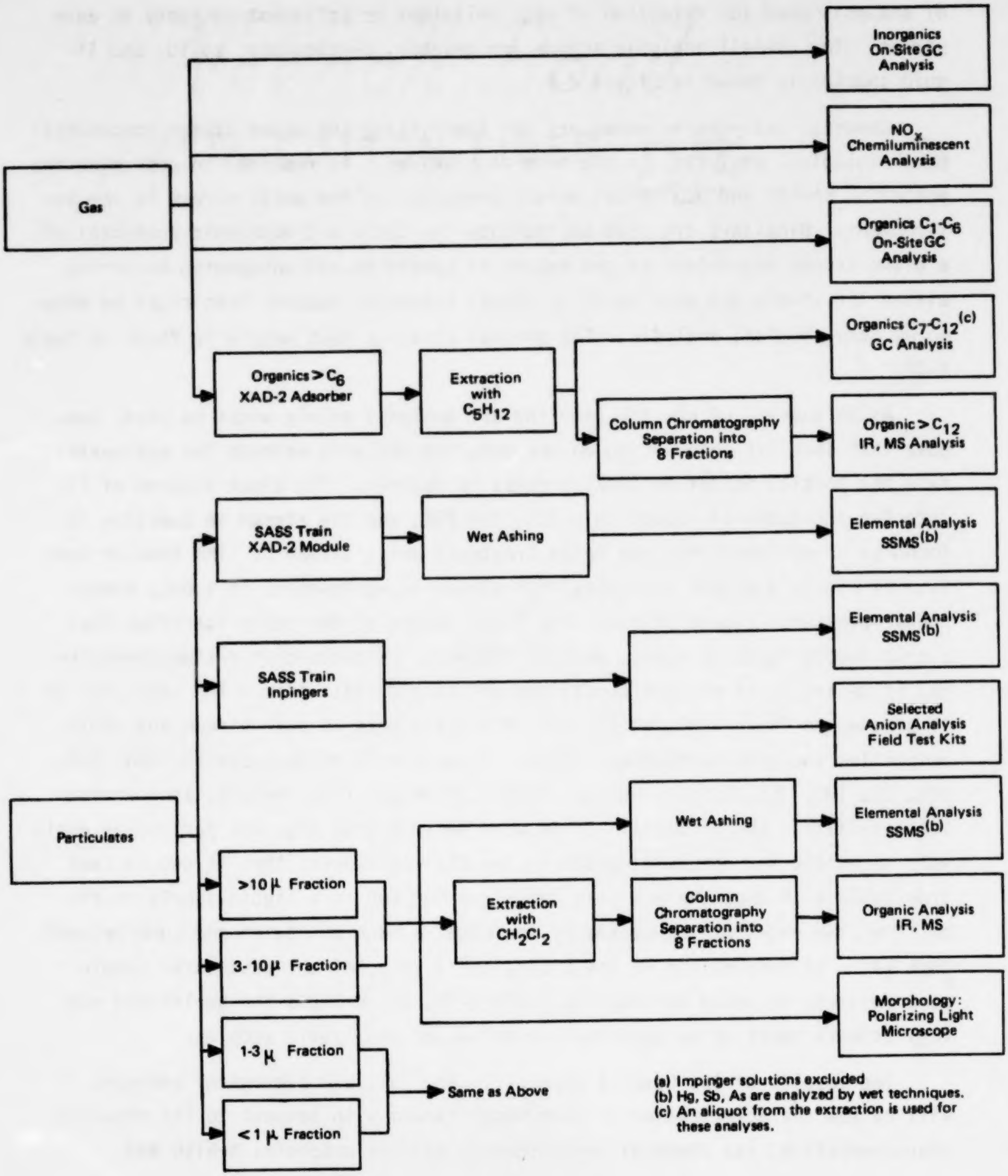
1. Gas Chromatography (GC)
2. Liquid Chromatography (LC)
3. Infrared Spectrometry (IR)
4. Low Resolution Mass Spectrometry (LRMS)
5. Spark Source Mass Spectroscopy (SSMS)
6. Atomic Absorption (AA)
7. CH_2Cl_2 Extraction
8. Chemiluminescence
9. Hach or Bausch and Lomb reagent test kits
10. Wet Chemical Analysis Techniques
11. Turbidimetric method for sulfates
12. Brucine-nitrate procedure
13. Combustion Titrimetric/Spectometric method

of analysis used for detection of each pollutant or pollutant category in each stream. The overall analysis scheme for gaseous, particulate, solid, and liquid samples is shown in Figure 4-9.

Chemical analysis is necessary for identifying the waste stream components; but, biological analysis, in the form of bioassays, is required to determine the potential health and ecological hazard presented by the waste stream to the environment. Bioassays are used to indicate the toxic and mutagenic potential of a given stream regardless of the amount of synergism and antagonism occurring within the stream and thus serve to reveal potential hazards that might be missed by pure chemical analysis. The minimal bioassay test matrix is shown in Table 4-32.

As an example of how the sampling and analysis matrix might be used, suppose that specific information on the sampling/analysis methods for wastewater from the partial oxidation (POX) process is desired. The block diagram of Figure 4-6 indicates all sampling points for POX, and the stream in question is found as an effluent from the water treatment unit, stream 3. The tabular section of Figure 4-6 then indicates that stream 3, wastewater, is a hot, atmospheric-pressure, liquid stream. The final column of the table specifies that a grab sample is to be taken, and the footnote indicates that a time-composite may be desirable if process conditions are varying with time. The next step is to proceed to Table 4-29, which lists the pollutants in each stream and their respective analysis techniques. Thus, stream 3 will be analyzed for HCN, BOD, COD, DO, TDS, TSS, Carbon, Hg, As, Sb, Cl, F, other trace metals, ash/particulate, sulfates, and nitrates. If it were desirable to know the particular analysis technique for determining BOD in the POX wastewater, then it can be seen from Table 4-29 that the analysis technique for BOD in a liquid sample is #9, or, from the notes at the bottom of the page, a Hach or Bausch and Lomb reagent test kit. If information on the biological testing of the wastewater sample were desired, it would be found in Table 4-32, which lists the health and ecology effects tests to be performed on all water and liquid samples.

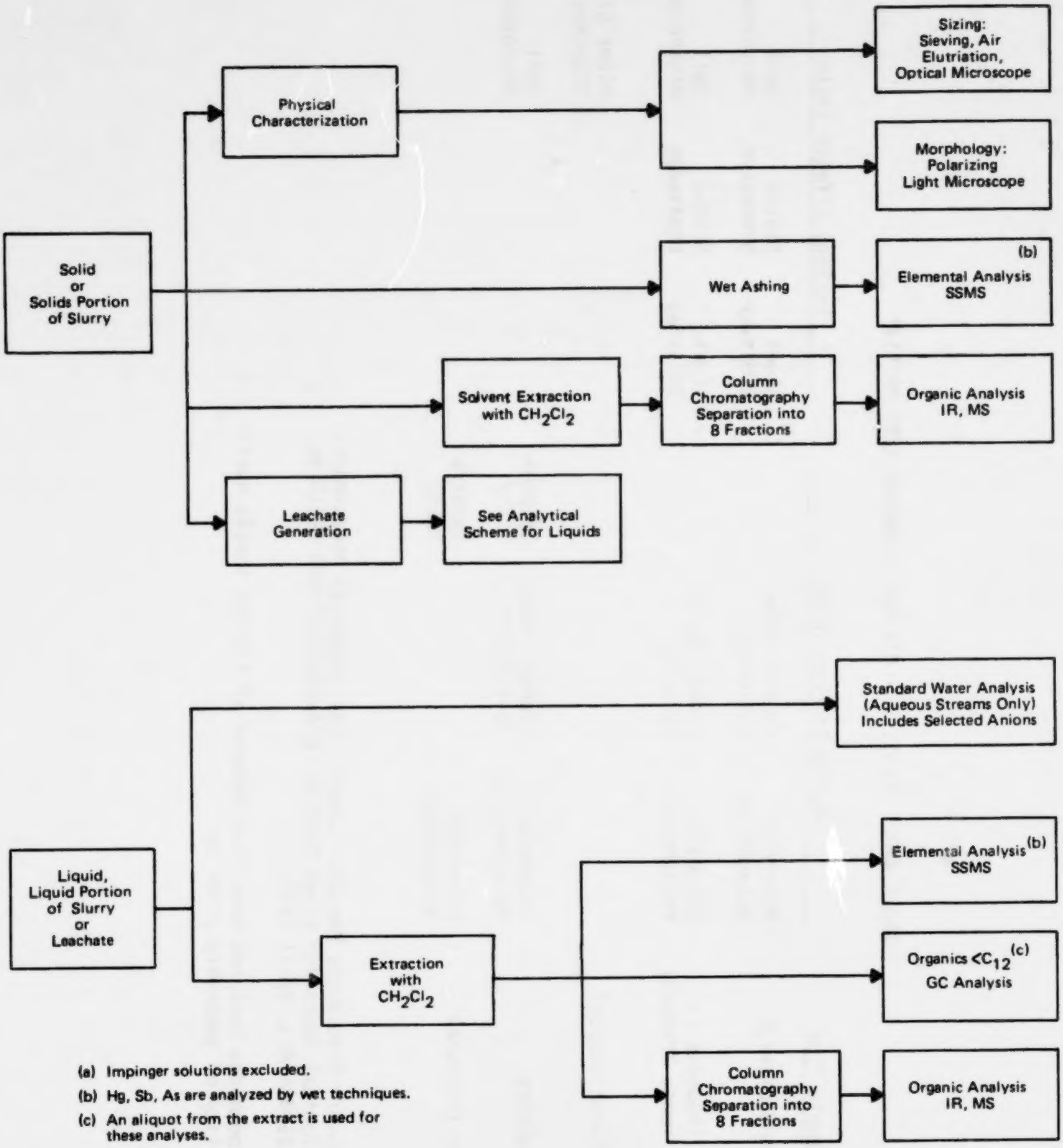
The results of the Level 1 physical, chemical, and biological analyses will be the characterization of each waste stream with respect to its physical characteristics, its chemical constituents, and its potential health and


Gas
Inorganics On-Site GC Analysis
NO$_x$ Chemiluminescent Analysis
Organics C_1-C_6 On-Site GC Analysis
Organics C_7-C_{12}(c) GC Analysis
Organics > C_6 XAD-2 Adsorber
Extraction with C_6H_{12}
Column Chromatography Separation into 8 Fractions
Organic > C_{12} IR, MS Analysis
SASS Train XAD-2 Module
Wet Ashing
Elemental Analysis SSMS(b)
SASS Train Inpingers
Elemental Analysis SSMS(b)
Selected Anion Analysis Field Test Kits
Particulates
Wet Ashing
Elemental Analysis SSMS(b)
>10 µ Fraction
3-10 µ Fraction
Extraction with CH_2Cl_2
Column Chromatography Separation into 8 Fractions
Organic Analysis IR, MS
Morphology: Polarizing Light Microscope
1-3 µ Fraction
< 1 µ Fraction
Same as Above

(a) Impinger solutions excluded
(b) Hg, Sb, As are analyzed by wet techniques.
(c) An aliquot from the extraction is used for these analyses.

Figure 4-9 - Overall Analytical Scheme for Level 1*

*"Procedures Manual for Environmental Assessment of Fluidized-Bed Combustion Process," EPA-600/7-77-009, January 1977.


Solid or Solids Portion of Slurry
Physical Characterization
Sizing: Sieving, Air Elutriation, Optical Microscope
Morphology: Polarizing Light Microscope
Wet Ashing
Elemental Analysis SSMS (b)
Solvent Extraction with CH_2Cl_2
Column Chromatography Separation into 8 Fractions
Organic Analysis IR, MS
Leachate Generation
See Analytical Scheme for Liquids
Liquid, Liquid Portion of Slurry or Leachate
Standard Water Analysis (Aqueous Streams Only) Includes Selected Anions
Extraction with CH_2Cl_2
Elemental Analysis (b) SSMS
Organics $<C_{12}$ (c) GC Analysis
Column Chromatography Separation into 8 Fractions
Organic Analysis IR, MS

(a) Impinger solutions excluded.

(b) Hg, Sb, As are analyzed by wet techniques.

(c) An aliquot from the extract is used for these analyses.

Figure 4-9 - Overall Analytical Scheme for Level 1. (Concluded)

TABLE 4-32. LEVEL 1 - MINIMAL BIOASSAY TEST MATRIX*

Sample Type	Health Effects Tests			Ecology Effects Tests		
Water and Liquids	Microbial Mutagenesis	Rodent Acute Toxicity		Algal Bioassay	Static Bioassays	Soil Microcosm
Solids (Aqueous Extract, Feed, Product, Waste)	Microbial Mutagenesis	Rodent Acute Toxicity		Algal Bioassay	Static Bioassays	Soil Microcosm
Gases (Grab Sample)						Plant Stress Ethylene
Particulates	Microbial Mutagenesis	(Rodent Acute Toxicity)**	Cytotoxicity			Soil Microcosm
Sorbent (Extract)	Microbial Mutagenesis		Cytotoxicity			

* IERL-RTP Procedures Manual: Level 1 Environmental Assessment, Biological Tests for Pilot Studies, EPA-600/7-77-043 (NTIS No. PB 268484/AS), April 1977.

** Recommended test not specified because of limited sample availability of secondary priority.

ecological hazards. This information is then used to define the Level 2 sampling/analysis program.

4.3 SUMMARY

Environmental data acquisition in this study involves an emissions inventory and test program development. The emissions inventory defines emissions loadings based on presently available data and identifies data gaps. The test program has been developed to define the data needed for assessing effluent characterization.

Test program development addresses the heart of control technology assessment, which is the actual collection of emissions data and establishment of pollutant loadings by sampling and analysis. A test program has been developed with the goal of completing Level 1 and Level 2 sampling requirements in one trip, so that the option of performing Level 2 analyses in the lab is retained.

A complete sampling and analysis matrix for each process under study has been developed, which indicates all streams to be sampled, the methods to be used for gathering the samples, stream conditions at the sampling point, potential pollutants in each sample, and the analysis techniques for quantifying pollutants concentrations. It is felt that this innovative sampling/analysis matrix format presents sufficient information in such a form that it could be used as the basis for a pre-site survey.

Thus, emissions loadings, as determined by sampling and analyses results and supplemented by theoretical engineering analysis, form the foundation upon which control technology assessment is based.

Emissions inventory includes definition of all process inputs and outputs based on theoretical engineering analysis and available sampling and analysis results. A composite residual oil has been developed, based on both imports and domestic sources, which is representative of a typical residual oil utilization process feedstock, and will provide a consistent basis for comparison between control system performances. A complete, reliable limestone analysis has also been selected to facilitate comparability between processes using a limestone sorbent. A theoretical engineering analysis has been initiated, the goal of which is to estimate pollutant loadings from residual oil utilization processes (utility boiler without controls, regenerable FGD, non-regenerable FGD, partial oxidation, hydrodesulfurization, and the CAFB process) based on the oil and sorbent inputs just mentioned.

Computerized equilibrium calculation-based predictions of combustion products are being used as the foundation for the estimation of inorganic pollutant loadings by theoretical engineering analysis. Due to a lack of thermodynamic data on organic compounds, only 12 organic species are presently considered as combustion products by the Battelle computer program being used. Benzene ring and small hydrocarbon predictabilities are good, but the major use of the program will be for prediction of inorganic species. Preliminary estimations of pollutant loadings have been made for each process by an extrapolation from previously published computerized equilibrium calculation results for a residual oil-fired boiler without controls. Computer runs for each process, at specified conditions, are planned, and some of the inputs have already been prepared. Results of the engineering analysis will supplement Level 1 sampling and analysis by serving (1) as a check on sampling and analysis results, and (2) as a source of compound-specific emission information in areas where Level 1 sampling and analysis results identify only the class, or category, or pollutant in a particular stream. The preliminary results indicate that, in all probability, only a few inorganic pollutant compounds, such as those of vanadium, nickel, and chromium, will pose any significant hazard in residual oil process gaseous effluents, but that most of the potentially hazardous pollutants will be emitted as a component of the wastewater or sludge streams.

A very limited amount of actual emissions data is available in the form of spark source mass spectrographic analyses of grab samples of FGD sludges and pelleted carbon residue from a partial oxidation unit taken last year in Japan Obviously, then, the need for additional sampling and analysis for environmental data acquisition is great.

SECTION 5

CONTROL TECHNOLOGY ASSESSMENT

In the environmental assessment of residual oil utilization, control technology background information, which will be used in evaluating the process techniques under study, has been compiled. Control systems and disposal options information has been reviewed and compiled based on known potential pollutants from residual oil combustion and upgrading operations.[7] An economic evaluation technique has been developed so that the cost effectiveness among various processes might be studied. For the common control techniques, pollutant control system studies have been made in order to compare the applicable concentration range and removal efficiency of potential control technologies for oil conversion wastestreams.

Although background information can be used to assess the economic and process operation studies, results from actual sampling and analysis must be used to assess the control technologies from an environmental standpoint. Reliable environmental data is a prerequisite for completion of the control technology assessment of residual oil processes.

5.1 POTENTIAL CONTROL TECHNIQUES

There are numerous potential multimedia pollutants from residual oil processing for which emission control regulations may be developed and implemented over the next 10 years. Some of the regulations will obviously receive greater attention and will be implemented earlier than others because of their environmental impact. The potential pollutants from residual oil processing systems are found in all media, in wide concentrations, and in various forms. Table 5-1 shows the diverse physical forms which the multimedia pollutants take in four major process categories (FGD, HDS, CAFB, and POX). Some major pollutants in residual oil, such as sulfur, may appear as different compounds in all phases of each process category. Others will only be associated with one process or phase.

TABLE 5-1. PHYSICAL FORMS OF MULTIMEDIA EFFLUENTS FROM RESIDUAL OIL UTILIZATION PROCESSES

Process	Air	Water	Solid Waste	Noise
FGD	Stack gas Particulate Fugitive	Runoff Slurry	Sludge handling and disposal	Noise (limestone preparation) Heat (stack)
HDS	Flue gas Particulate Fugitive HC Vents	Sour water Filter backwashs Spills	Catalysts handling Spent cat. disposal Filter backwash disposal	Hydrogen manufacture Noise (compression) Heat (flares, furnaces)
CAFB	Flue gas Particulate Fugitive Vents	Runoff	Ash Spent stone Fugitive (coal and limestone	Noise (solids transport) Heat (flares, furnaces)
POX	Flue gas Particulate Vents Fugitive	Sour water C/gas separation	Ash Spent catalyst	Noise (compression) Heat (flare)

For the control of pollutants in air (first column of Table 5-1), there are several effective and widely-used techniques which may be used to attain the effluent quality desired. Some of the potential control technologies being considered for the control technology assessment for air are listed below:

- Gravitational/mechanical collector
- Media filtration (e.g., baghouse, fabric filter)
- Adsorption (e.g., carbon)
- Absorption (scrubber)
- Condensation
- Electrostatic precipitation
- Incineration

Pollutants in a water stream are the most common final disposal or treatment problems, because the compounds in air and solids often end up in wastewater streams from scrubbers or in runoff from solids storage areas. The following treatment steps have been considered for the control technology assessment for water:

- Rainwater run-off collection
- Equalization/Neutralization
- Gravitational (API) oil/water separator
- Dissolved air flotation
- Coagulation/flocculation
- Biological filtration (trickling filter)
- Activated sludge system (including aeration basins, clarifiers, and sludge recycle)
- Granular media filtration
- Carbon adsorption
- Stripping

The potential solids and sludge treatment techniques generally accepted for residual oil processing systems are listed below:

- Catalyst regeneration
- Sludge thickening
- Vacuum filtration
- Chemical fixation
- Fluid-bed incineration
- Land filling/land farming

Heat recovery, noise, and thermal pollution are generally difficult to abate. With process modification and source isolation and insulation, however, the pollution could possibly be reduced to a minimum.

An optimum or cost-effective pollution control strategy is always case dependent. Source characteristics, desired goal, and best available technology are the factors which will dictate the most attainable environmental quality. Cost limitations usually play an important role in setting a most probable environmental goal; and, consequently, a most practical control strategy is determined by a risk and benefit analysis.

Potential control systems and disposal options for known pollutants from residual oil combustion and upgrading operations are tabulated in Table 5-2. In general, the treatment methods listed are commonly practiced in the refinery and utility industries. For each pollutant listed, a control technology study has been made to compare the treatment methods and their limitations for use. For each treatment method, the applicable effluent concentration and expected removal efficiency are also listed.

Some of the pollutants listed in Table 5-2 are more likely to pose an environmental problem in certain processes than in others. For example, cyanide and ammonia are more likely to be major concerns in POX and HDS wastewater, while vanadium and other heavy metals are of concern in these processes, as well as FGD and CAFB. Phenols have been noted as a possible problem in POX wastewater; and pollutants, such as suspended solids and tar and oil, will be of concern in every residual oil utilization process under study.

Particulate matter in the gaseous emission streams from residual oil

TABLE 5-2. POTENTIAL CONTROL TECHNOLOGY FOR RESIDUAL OIL PROCESS EFFLUENTS

Water Pollutants	Treatment Method	Limitations	Applicable Concentration Range	Removal Efficiency
Cyanide	(1) Decomposition to CO_2 and N_2 via cyanate with chlorine at pH 8-8.5	Toxic cyanogen chloride may be liberated, a large excess of chlorine is required	100-1000 mg/l	100%
	(2) Electrolytic decomposition to CO_2 and N_2 via cyanate at 200°F	Interference by sulfate	$>$ 1000 mg/l	99.9% after 7-18 days
	(3) Ozonation	Only partial decomposition to CO_2 and N_2	100-1000 mg/l	100%
Fluoride	(1) Precipitation with lime as calcium fluoride at pH 11	Slow rate of precipitation	720 mg/l	97-99%
	(2) Coagulation by alum	Applicable only to low hardness water	$<$ 20 mg/l	95%
	(3) Adsorption on hydroxylapatite bed	Presence of chlorine increases cost of bed regeneration	$<$ 20 mg/l	92-98%
Tar and Oil	(1) Gravity separation	Does not remove emulsion	Primary treatment	60-99% of floated oil
	(2) Centrifugation		Secondary treatment	--
	(3) Coagulation or demulsification with chemicals, followed by air flotation or settling	Addition of alum forms sludge which are difficult to dewater	Secondary treatment	50-90%

(continued)

TABLE 5-2 (Continued)

Water Pollutants	Treatment Method	Limitations	Applicable Concentration Range	Removal Efficiency
Tar & Oil (cont'd.)	(4) Biological treatment		Secondary treatment	Removal to 15 mg/l
Phenols	(1) Pulsed column extractors		> 500 mg/l	94%
	(2) Light oil extraction (Koppers)		> 1500 mg/l	98-99.3%
	(3) Incineration		> 7000 mg/l	100%
	(4) Activated carbon bed		< 50 mg/l	> 99%
Suspended Solids	(1) Sedimentation			90-95%
	(2) Chemical coagulation			95-99%
	(3) Filtration			95%
Ammonia	(1) Stripping at pH of 10-11	Water adsorbs CO_2-may lead to scale formation		50-90%
	(2) Biological nitrification	Nutrient may be required	< 1250 mg/l	> 99%
	(3) Ion exchange			80-95%
Chloride	(1) Deep well injection		> 60 g/l	Ultimate disposal
	(2) Evaporation ponds	Limited by geographical location and land availability		100%
Sulfide	(1) Biological oxidation to sulfate			100%

(continued)

TABLE 5-2 (Continued)

Water Pollutants	Treatment Method	Limitations	Applicable Concentration Range	Removal Efficiency
Vanadium	(1) Ferric hydroxide adsorption		< 800 mg/l	99%
Heavy Metals (Cr, Cu, Ni)	(1) Lime and settle	Reduction is not complete. Rate depends on pH, reducing agent, and contact time	100-500 mg/l	> 99%
	(2) Sulfex^{TM}	High initial investment	1-500 mg/l	95-98%
Air Pollutants				
Particulate	(1) Cyclone	High pressure drop (4-40 in. W.G.)		80-90%
	(2) Tornado	High pressure drop (30 in. W.G.)	< 30 gr/SCF	93-97%
	(3) Bed filter		< 40 gr/SCF	90%
	(4) Electrostatic precipitator	High energy consumption		99%

Source: Robson, F. C., and W. A. Blecher (UTRC) and C. B. Colton (Hittman Associates, Inc.), "Fuel Gas Environmental Impact," EPA-600/2-76-153, June, 1976.

utilization processes generally contains much of the trace metals present in the oil feed, as well as acid aerosol emissions such as H_2SO_4 from FGD processes, which may be adsorbed by the particulate. Thus, these pollutants are not listed as separate air pollutants, since the same treatment processes applicable to particulate control are effective for trace metal and acid aerosol removal as well.

Table 5-2 will be expanded as additional treatment technologies are developed or additional problem pollutants are revealed, or reduced if potential pollutants now on the list are found to exist in the effluent in concentrations too small to present environmental or health hazards.

5.2 RESIDUAL OIL UTILIZATION TECHNOLOGY

As a result of the expected standards setting activities for new and existing residual oil processes, pollutant control techniques are being developed and implemented to meet future standards. A large fraction of current pollutant control applications in the utility industry use flue gas scrubbing as a post-combustion treatment. Other approaches such as upgrading fuels, as well as more advanced combustion and oil processing, are being evaluated for more extensive potential future use. The applicability and effectiveness of residual oil utilization technology depend on the specific equipment and characteristics of the fuel used.[29] The progress made in residual oil utilization processing is a function of the importance of the source in local and national pollutant regulatory strategies.

The following paragraphs summarize the technical problems and environmental needs of the major residual oil utilization technologies based on the discharge stream sources.

Solids Pretreatment

The crushing, sizing, handling, drying, and storage of limestone and other solids pretreatment are characterized by fine particulate emissions and some aqueous effluents from water runoff. The most common dust control technologies use hoods, cyclones, bag houses, or electrostatic precipitators. Simpler dust control problems are handled using water sprays followed by primary wastewater treatment for the aqueous effluents. In some cases where solids drying results in organic air emissions, hydrocarbon control using afterburners or carbon adsorption may be used. In general, for the particulate problems in solids pretreatment, data from cement plants and particulate control devices should be directly applicable. However, only limited data are available for the control of hydrocarbon emissions.

Oil Gasification

No data is available on characteristics of vent gas emissions from the various oil feeding and ash removal devices; but, the applicable control technologies include particulate collection, incineration, and recycle. There is a serious need for data on the amounts and types of organics, H_2S, COS, SO_2, HCN, NH_3, and trace elements for start-up vent streams. The ash from residual oil gasification may be treated by chemical fixation, used in some by-product applications, or placed in a landfill. Although limited data are available on ash solid waste disposal, data on organics, unreacted carbon, and trace elements, along with leaching tests, are needed. Data is also needed on suspended and dissolved organics and inorganics for ash quench water recycle and treatment processes.

Gas Purification

For residual oil processes which have a product gas, there are three discharge stream sources requiring intermediate pollutant control technology. (1) Cyclones and electrostatic precipitators are applicable for removing and collecting particulates. The performance of particulate removal devices is highly dependent on the loadings, size distribution, and physical characteristics of the collected particulates. Limited data are available on these streams, but additional data are needed to determine collection efficiencies. (2) Gas quenching and cooling involves stream characterizations for collected tar and particulates from the gas and spent quench liquor. Data from spray towers and exchangers are needed to determine the removal efficiencies for particulates, tars, oils, and trace elements. Spent quench liquor effluent may contain suspended organics, inorganics, and trace elements which will affect the loading for recycle and waste water treatment processes. (3) Chemical or physical sorption and direct conversion processes are used in removing acid gases. Data are needed to determine the acid gas removal efficiency, the sorbent or solvent degradation characteristics, and blowdown. Some limited data have been reported on most acid gas removal processes used to treat low-

and medium-Btu gas.

Air Pollution Control

The methods of controlling particulate emissions such as cyclones, electrostatic precipitators, baghouses, and wet scrubbers are currently available; however, data are needed to determine an effective means of collecting these emissions so that they may be treated by typical particulate control techniques. Limited data are available on most direct conversions and Claus tail gas cleanup processes for treating sulfur-laden gases. Hydrocarbon control data via afterburners and carbon adsorption is not available in enough detail to project the hydrocarbon removal effectiveness and sorbent and catalyst degradation characteristics.

Water Pollution Control

Numerous discharge stream sources fall into this operational category, including oil/water separation, suspended solids removal, and dissolved organics and inorganics removal. Filtration, separation, and flocculation-flotation are generally used to segregate sludges and oily scum from wastewater streams. Liquid extraction, oxidation, and carbon adsorption are used to remove dissolved organics. Acid gas and ammonia may be stripped from sour water, but the by-product tail gases must be treated further. Other dissolved inorganics may be removed by forced evaporation.

Solid Waste Control

Ash, sludge, spent sorbents, and spent catalysts must be incinerated, chemically fixed, and/or used as landfill. Ultimate disposal of these solid wastes depends to a large extent on the results of leachate tests for trace elements and dissolved toxics. For example, a major problem associated with non-regenerable scrubbers is the tremendous amount of waste material that must be disposed of in an environmentally-acceptable manner. In some cases, credits may be taken for usable solid wastes to make the control technology more cost effective; but, in the U. S., most sludge produced from scrubbers requires disposal.

5.3 ECONOMIC COST MODEL DEVELOPMENT

An economic evaluation of a chemical process can be typically categorized into four major steps. The first step is flow plan preparation; the second step is equipment sizing; the third step is cost estimation, including direct cost and indirect cost; and, finally, the fourth step is feasibility measures evaluation involving calculation of payout time, discounted cash flow, return on investment and annualized cost in the case of non-profit generating investment, such as pollution control devices.

Although many methods and procedures currently being used are effective for costs estimation purposes, they do not provide a common basis for comparison as to evaluation of economic feasibility or cost effectiveness among various processes under investigation. It is necessary that an economic analysis of pollution control and energy production operations should be conducted uniformly based on a standardized procedure and consistent data bases. In fact, several attempts have been made within government agencies to propose such a procedure. The criteria used for the procedure selection are based on reliability, uniformity, and acceptability of a method which will allow for ready comparison among different processes. Figure 5-1 shows several technical economic evaluation schemes. The first two steps of an economic evaluation, the flow plan preparation and equipment sizing, are not included in Figure 5-1.

Table 5-3 lists work flow, procedures/guidelines and results of a standard procedure of economic evaluation selected for pollution control operations. This scheme will be followed in the environmental assessment of residual fuel oil utilization study to conduct cost analyses of various modes of oil utilization. Work flow in a typical economic evaluation is depicted in the first column of Table 5-3. Each block represents a major step in the entire evaluation scheme. The guidelines and procedures needed to perform the work dictated by each step, together with its data sources, are listed in the second column (Table 5-3). The third column of Table 5-3 indicates the results or outcomes of each major step. Characteristics and information and data requirements of five basic cost estimation types are given in Table 5-4. Recommended methods with estimation accuracy range are also included in Table 5-4. Detailed information requirements for preliminary cost estimation of major process equipment are indicated in Table 5-5.

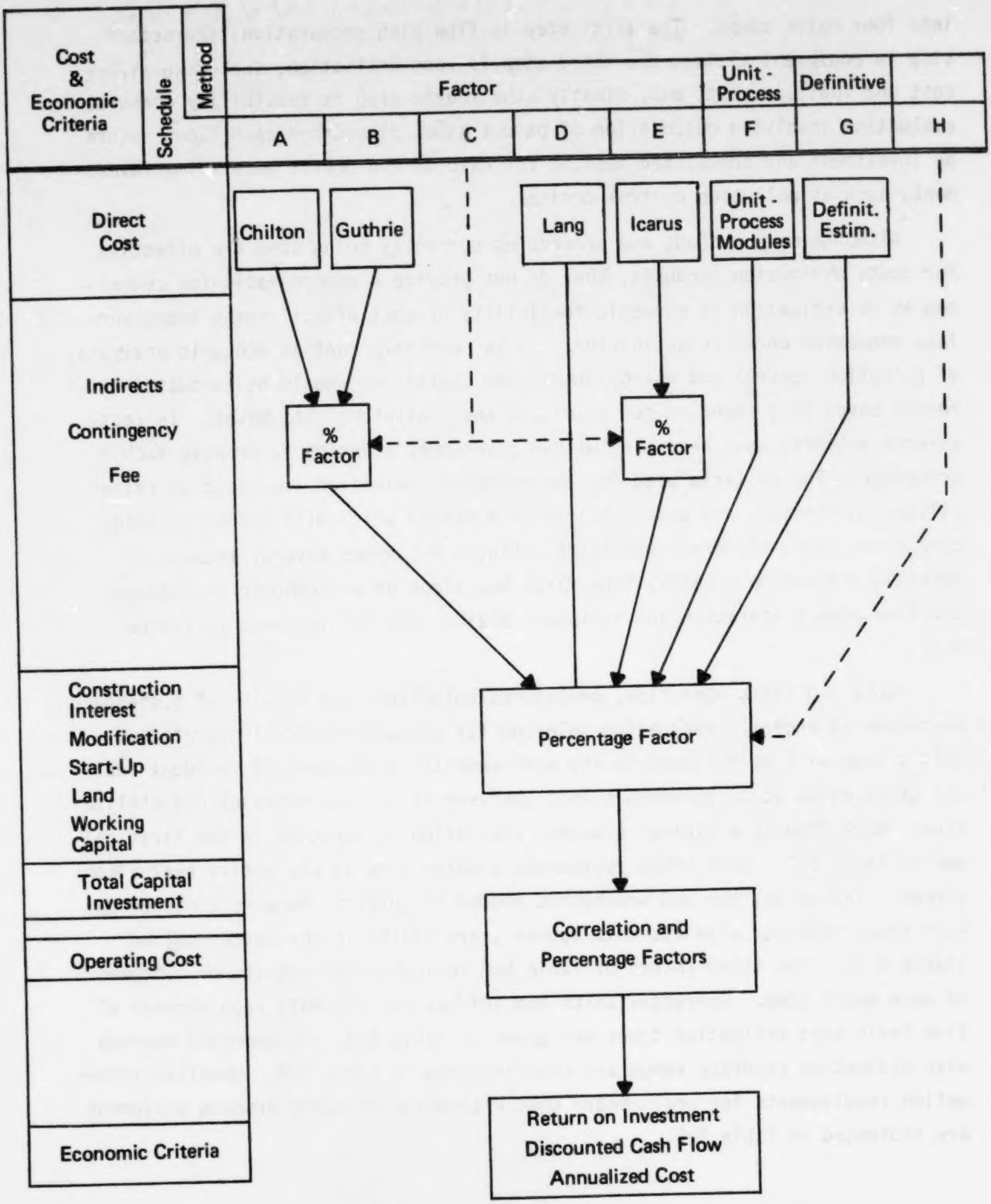
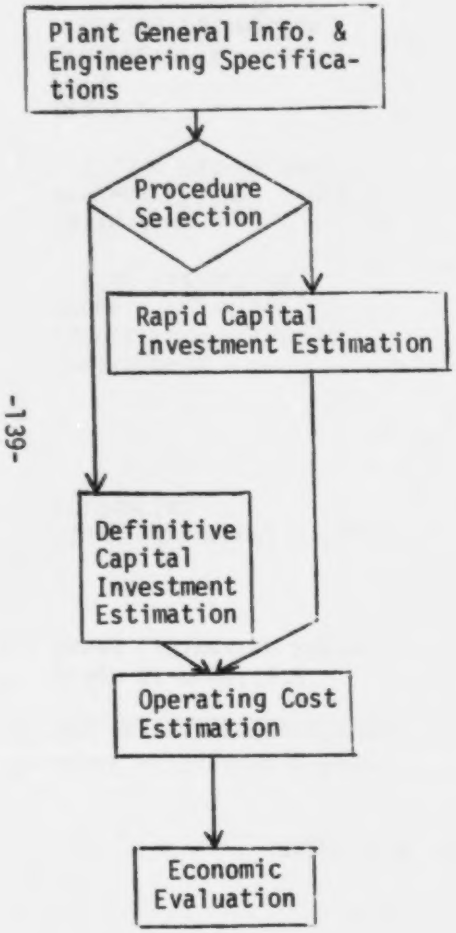


Figure 5-1 - Typical Economic Evaluation Schemes

TABLE 5-3. STANDARD PROCEDURES OF ECONOMIC EVALUATION FOR POLLUTION CONTROL OPERATIONS



Work Flow Chart	Guideline, Procedure and Data Source	Result
Plant General Info. & Engineering Specifications	Process Design	Plant Capacity, M&E Balances, Flow Plan, Equipment List
Procedure Selection	Level of engineering effort	Cost model/procedure to use
Rapid Capital Investment Estimation	Licensor or vendor information Unit-price method Exponential (0.7 power) rule Lang factor; Chilton factor Guthrie Scheme EPA reports	Total capital investment required or Major Plant Items (MPI) cost with accuracy of estimation
Definitive Capital Investment Estimation	Vendor information M. W. Kellogg cost model Guthrie Scheme Proprietary data/computer programs	Major Plant Items (MPI) cost with accuracy of estimation
Operating Cost Estimation	M. S. Kellogg model Chemical Engineering Handbook EPA reports Proprietary data/computer programs	Operating cost and other expenses
Economic Evaluation		Total capital investment required, Feasibility measures, i.e., ROI, POT, DCF & UAC

TABLE 5-4. DEFINITION AND GUIDELINES OF FIVE BASIC ESTIMATION TYPES

Types of Estimates (each has several designations)	Method	Information Requirement/ Estimates Characteristics	Accuracy
Order-of-Magnitude - Rapid Estimation Ratio	Unit price; .7 power function relationships	Based on market survey or rough feasibility study (plant capacity, unit-price curves), gives preliminary indication of feasibility	± 50%
Study (factored) - Rapid Estimation	Lang, Chilton, Guthrie Scheme	Based on study design effort (simplified flow plan with rough M&E balances), provides guidance for further considerations and project studies	± 40%
Preliminary Budget Authorization Scope - Rapid/Definitive Estimation	Lang, Chilton, Guthrie Scheme	Sufficient data (flow plan, equipment list) are available on which to base estimate that results can be used to make budget decision	± 20-30%
Definitive Project Control - Definitive Estimation	Detailed item-by-item, step-by-step estimation	More complete data are available but short of completed specifications and drawings	± 10%
Detailed Firm Contractor's - Definitive Estimation	Detailed item-by-item, step-by-step estimation	This estimate is based on complete specifications, drawings, and site surveys	± 5%

TABLE 5-5. INFORMATION REQUIREMENTS FOR PRELIMINARY COST ESTIMATION

Major Process Equipment	Capacity/Description						Mechanical Design		Material of Construction
	lb/hr or GPM or CFM or Total Vol.	Btu/hr. or Surface Area	Head or MP	Type	Dia.	Height or Length	DT, Design Temp.	DP, Design Pres.	
Fired Heaters & Boilers		X		X			X	X	X
Stacks					X	X			X
Reactors & Internals (catalysts)	X			X	X	X	X	X	X
Towers & Internals (trays, packing)				X	X	X	X	X	X
Heat Exchange Equipment		X		X			X	X	X
Cooling Towers (cells, temp.)	X		X						
Vessels & Drums	X						X	X	X
Pumps & Drivers	X		X	X			X	X	X
Blowers & Compressors	X		X	X			X	X	X
Elevators, Conveyors, Mat'l. Handling Equipment	X		X	X		X			X
Tankage	X			X	X	X	X	X	X
Filters, Centrifuges, Sep. Equipment	X	X		X			X	X	X
Agitators & Mixers			X	X					X
Scrubbers & Entrainment Separators (Internals)	X		X	X			X	X	X

(continued)

TABLE 5-5 (continued)

Major Process Equipment	Capacity/Description						Mechanical Design		Material of Construction
	lb/hr or GPM or CFM or Total Vol.	Btu/hr. or Surface Area	Head or HP	Type	Dia.	Height or Length	DT, Design Temp.	DP, Design Pres.	
Machine Tools & Machine Shop Equipment									
H.V.A.C., Dust Control (Process Only)	X		X	X			X	X	X

Note: Range of accuracy for preliminary estimation is ± 25%.

The Lang factor method should be considered only for checking purposes. The Chilton method may be the most useful factor method and usually is excellent for checking purposes. The Guthrie scheme is the most involved factor method and should yield reliable results. The Guthrie scheme could sometimes be employed as a definitive estimation method, provided that correlated cost data and good Guthrie factors are available. The ICARUS data manual presents, in convenient graphical and tabular form, cost information for installed equipment item modules for pollution control facilities. The unit-process modules method is appropriate for liquid waste treatment plants, e.g., municipal sewage treatment.

The accuracy associated with a cost estimation is closely related to cost data availability and the level of process engineering effort. Often, an adequate process engineering work to achieve certain degrees of accuracy of estimation on a process in question might not always be done. Often, it is possible to develop only a rough estimate. Minimum data required to allow a rapid estimation are sometimes lacking, especially for pollution control operations. On the other hand, good engineering work may be available from owners of processes, e.g., POX, HDS, and CAFB. In some cases, however, an "isolated" process cannot always be found in typical industrial applications; e.g., waste streams from POX and HDS are generally integrated with a centralized or combined waste treatment plant. Cost information on this type of process could only be obtained by flow rate proration.

Hence, potential problem areas in carrying out the entire economic evaluation for pollution control operations are:

(1) inadequate engineering work for the accuracy desired,

(2) scarcity of raw cost data, and

(3) lack of readily-usable engineering data/information resultant from industry's combined waste treating practice employed in a complex chemical processing plant, e.g., refinery operations.

Catalytic's approach to these problems involves the development of standard procedures of economic evaluation, uniform data bases, and adequate engineering effort.

Much effort has been devoted to the development of standard procedures and uniform cost data bases, and considerable progress has been made. However, progress on the development of adequate process engineering work regarding some residual oil utilization processes of interests, e.g., HDS and POX, has been limited. The lack of progress in this area is due to the scarcity of a comprehensive waste streams inventory and characterization, and, to a lesser degree, to the incompleteness of process information resultant from industry's reluctance or inability to yield an adequate set of process data and information. Nevertheless, good progress has been made in the development of process information regarding the commercialized residual oil utilization processes. It is believed that adequate process engineering work for carrying out the desired economic analysis could be developed as soon as comprehensive emissions data become available. This will be a result of the current effort on waste streams characterization as part of this environmental assessment project.

5.4 SUMMARY AND CONCLUSIONS

In light of the fact that emission control regulations are likely to be developed in the next ten years for numerous multimedia pollutants from residual oil utilization processes, it is important that the existing and/or developing control systems and disposal options be evaluated and compared from both technological and economic standpoints. Environmental impact of the various control options will be assessed based on actual sampling and analysis results. Economic evaluation is to be based on a standardized procedure and consistent data bases.

Control techniques have been enumerated for air, water, and solids/sludge effluents, which may vary widely in such important parameters as control efficiency, energy usage, applicable concentration range, and costs; but, an optimum or cost-effective pollution control strategy is always case dependent.

Large data gaps still exist in many of the control technology assessment areas. The areas included are listed below:

- Limited data are available for hydrocarbon emissions from solids pretreatment.

- No data are available on characteristics of vent gas emissions from the various oil feeding and ash removal devices in oil gasification.
- Data are needed on organics, unreacted carbon, trace elements, and leaching tests for ash solid waste disposal from oil gasification.
- Data are needed on suspended and dissolved organics and inorganics for ash quench water recycle and treatment processes from oil gasification.
- Limited data are available on particulate removal by cyclones and electrostatic precipitators for product gas purification.
- Spray tower and exchanger data are needed to determine removal efficiencies for spent liquor from gas quenching and cooling which contains particulates, tars, oils, and trace elements.
- Limited data have been reported, but more are needed to determine acid gas removal efficiency, sorbent or solvent degradation characteristics, and blowdown from gas purification.
- Data are limited on most direct conversions and Claus tail gas cleanup processes for treating high sulfur gaseous emissions.

In order to develop the data necessary for control technology assessment, Catalytic shall conduct sampling and analysis activities, incorporating the Level 1 and Level 2 sampling and analysis methodologies adopted by EPA for five typical plants representing the following categories: combustion without controls; combustion with FGD; combustion with POX; HDS; and upgrade and HDS for low sulfur fuel oil. Development of the necessary data base will involve:

(1) Selecting a preferred plant site and an alternative site for each category;

(2) Obtaining cooperation and entry permission into each preferred and alternate plant site;

(3) Designing the field sampling experiment;

(4) Conducting a pre-test survey, with participation by the subcontractor who will conduct the field testing and laboratory analysis;

(5) Conducting a field test;

(6) Conducting a chemical laboratory analysis; and

(7) Preparing an environmental assessment sampling and analysis document.

No problems are anticipated beyond the coordination of required auxiliary services and facilities, which have been costed out in detail based on previous sampling experience.

Available data indicate that spent catalyst resulting from the conversion of residual petroleum fuels is a potential source of environmental impact which should receive further attention. Accordingly, Catalytic shall:

(1) Investigate the current catalyst reprocessing and disposal options;

(2) Characterize the spent catalyst;

(3) Evaluate control/disposal options via thorough engineering and economic analyses; and

(4) Incorporate the results into the environmental assessment report.

In the absence of regulations and standards pertinent to compounds in the spent catalyst, toxicity information regarding the metallic compounds that could be formed under hydrodesulfurization conditions will be compiled and used as a basis for evaluation.

A series of parametric cost studies will be conducted to characterize one or more of the environmental control process variables having incremental effects on the direct production costs of the following process categories:

combustion with FGD; hydrodesulfurization; and combustion with POX. The procedure will be as follows:

(1) Review existing cost data;

(2) Determine the incremental costs of selected process variables related to environmental control;

(3) Recommend the best technologies economically achievable; and

(4) Prepare a parametric cost study document.

Many methods and procedures are currently available for effective costs estimation. A standardized procedure is to be selected based on reliability, uniformity, and acceptability of a method which will allow for ready comparison among different processes. The Chilton method may be the most useful factor method and usually is excellent for checking purposes.

Scarcity of raw cost data and lack of readily-usable engineering information are potential problems, but it is anticipated that development of standard procedures of economic evaluation, uniform data bases, and adequate engineering effort will alleviate these problems.

SECTION 6

ENVIRONMENTAL ALTERNATIVES ANALYSIS

6.1 SOURCE ANALYSIS MODEL (SAM)

In conducting environmental assessments, it is necessary to do one or more of the following tasks: (1) rank individual effluent streams by the expected toxicity of their discharges; (2) establish sampling priorities; (3) determine problem pollutants; (4) recommend best multimedia control technology alternatives; and (5) recommend control/disposal technology development programs. An objective of alternative analysis is, therefore, to compare environmental pollutant loadings from specific sources to Multimedia Environmental Goals (MEG).

Aerotherm Division of Acurex Corporation has prepared for EPA the simplest member of a sequence of Source Analysis Models (SAM's) of increasing complexity and thoroughness which can be used as a tool to help with the five tasks mentioned above.[1]

The use of a Source Analysis Model (SAM) for screening of control options provides the environmental assessment community with a workbook or format which identifies input data requirements and guides the user through a set of calculations. These calculations provide a quantitative means of assessing the pollution potential of a source and of control options.

The SAM format focuses on each separate effluent stream which arises during an energy production or industrial process. Such streams may exist because of the process itself, for example, flue gas and bottom ash emissions from a utility boiler, H_2S, mercury, and arsenic emissions from certain steam-dominated geothermal wells, and hydrocarbon emissions at petrochemical refineries. Streams may arise because of the application of pollution control technology to a process-generated effluent, such as, hopper ash from baghouses or electrostatic precipitators, and scrubber-generated sludge.

Each use of the SAM format assumes a specific set of effluent streams which exit from the process itself or from the control technology in use. The format then examines the extent or amount of environmental impact which results from utilizing information on specific substances of concern determined from EPA's (Levels 1 and 2) phased approach to comprehensive sampling and analysis.[6,7]

SAM's can be used to rank effluent streams. In this application, the SAM is used to compare the toxic-unit rate of discharge into each effluent stream; these toxic-unit summations can then be ranked by magnitude. Examination of the relative magnitudes generated by different streams immediately shows the relative hazard of the different effluent streams.

Another function of SAM's is the establishment of additional Level 2 and Level 3 sampling and analysis priorities in performing environmental assessments.

Potential problem pollutants and pollutant priorities may be determined by the SAM format. In this application, use of the SAM can lead to an understanding of the pollutants that are most likely to cause major environmental impact because they remain poorly controlled under all equipment options currently available.

SAM's can also determine the most effective control technology options. In this application, the SAM is used to examine a given process stream with first one and then another control approach. The impact of alternative control equipment choices can be compared on the basis of the differing reductions which can be expected to occur in the original process stream pollutant emissions, and the ways in which concentration of certain pollutants into particular control equipment effluent streams will occur.

Still another use of the SAM format is to determine the need for control/disposal technology development. Straightforward application of the proper SAM format can, therefore, be used to accomplish a variety of goals.

In the simplest SAM, designated "SAM/1A: A Rapid Screening Method for Environmental Assessment of Fossil Energy Process Effluents," effluent streams from any process or applicable controls are not assumed to interact with the external environment (i.e., transport of the components in the effluent stream to the external environment occurs without transformation of the components).

No assumption is made about pollutant-specific dispersion; but, it is assumed that such dispersion from the source to a receptor would, in almost all cases, be equal to, or greater than, the safety factors normally applied to acute (short-term exposure) toxicity data to convert them to estimated safe low-level, longer-term chronic ambient exposure levels. Furthermore, the premise that the MATE values are adequate and that no synergistic effects occur should also be assumed. The validity of these assumptions cannot be established on a case-by-case basis. In many cases, the assumptions are conservative. However, these factors should be kept in mind in evaluating the need for more detailed assessment.

Thus, SAM/1A is on an effluent concentration basis and uses only one potential assessment alternative (the MATE).

The general procedure to be followed when using SAM/1A for a given source and control option has been described and explained by Aerotherm. Such rapid screening requires understanding of the assumptions being made.

The user assumes that the $\sim$650 substances presently on the MEG list as potential components of an effluent stream are the only ones which need to be included and are known accurately enough. Unknown components may be sources of environmental impact which are modified or modifiable by the control technology and, therefore, Level 1 bioassay results will be important as a companion data base for interpretation of SAM/1A results.

Providing sufficient data to determine the need to reduce emissions from an industrial operation is one of the objectives of alternative analysis. The development of methodology for source assessment and analysis is still evolving and is a continuous effort for EPA. It can be expected that suitable models or methodology will be refined as experiences grow. Some kinds of alternative analysis (e.g., SAM/1A) to provide information for process ranking regarding sources/controls, pollutants, and regional siting will be carried out in the current work of environmental assessment on various residual oil utilization processes.

6.2 POLLUTANT PRIORITIZATION

Pollutant prioritization is an integral part of the environmental assessment methodology, as it is presently being developed by EPA. Figure 1-1 illustrates the overall environmental assessment/control technology development scheme, including pollutant prioritization as it fits into the environmental objectives development task.

Prioritization can be divided into two parts: preliminary prioritization and practical prioritization. Preliminary pollutant prioritization involves the comparison of "worst case" effluent concentrations of each potential pollutant with its respective Minimum Acute Toxicity Effluent (MATE) value and the ranking of pollutants by the resulting ratios. Practical pollutant prioritization consists of ranking potential pollutants by the ratio of their expected (rather than worst case) effluent concentration to MATE values, based on a practical engineering analysis of the combustion and control processes.

Practical experience with the prioritization methodology has been gained by its application to a lime slurry Flue Gas Desulfurization (FGD) system treating flue gas from a residual oil-fired boiler.

Prioritization is a screening method for determining which pollutants to examine first. Since time and money prohibit extensive study of the universe of potential pollutants, prioritization is used to determine priority pollutants for investigation, as the name implies.

Preliminary (worst case) prioritization is valuable as a method for reducing the number of pollutants to be considered in the detailed engineering analysis which follows as part of the practical prioritization. The expected effluent concentrations which result from the engineering analysis are used as input to test program development and identification of sampling and analytical techniques. Results of practical prioritization serve as a check list for sampling. Pollutant streams within a process can be prioritized using the expected effluent concentrations as calculated by the engineering analysis. Results of the engineering analysis may indicate potential problems and will supplement Level 1 sampling and analysis with details.

The first step in pollutant prioritization is to obtain detailed analyses of all system inlet streams. For the lime scrubbing of residual oil-burner flue gas, those streams are: residual oil, combustion air, lime, and water. For the worst case effluent concentrations, it is assumed that all inlet stream pollutants are completely discharged in the effluent and that each pollutant compound which could be formed from any combination of inlet stream constituents is formed to the maximum concentration possible, given the amounts of constituents available. For example, the worst case concentration of elemental nickel in the effluent is calculated assuming that all Ni in the inlet streams exists as elemental nickel. Similarly, the worst case concentration of nickel chloride in the effluent is calculated assuming that all Ni combines to form $NiCl_2$ (if enough Cl is available). Worst case emissions must be calculated for each media (air, water, and land). Obviously, the sum of the worst case effluents is greater than the amount of actual effluent leaving the system. Thus, the worst case analysis indicates every possible problem pollutant; but, the results are far from being a realistic description of the system effluent. Almost all pollutants indicated in a worst case analysis will exist in smaller concentrations than their worst case values (none will exist at higher concentrations), and many may not be detected at all in the actual effluent.

A ranking of potential pollutants based on the worst case analysis must include a factor of relative toxicity as well as concentration. MATE's, developed at Research Triangle Institute (RTI) from toxicological data such as TLV's, NIOSH recommendations, LD_{50}'s and LD_{20}'s, LC_{50}'s, TD_{Lo}'s, TL_m, Drinking Water Regulations, and Water Quality Criteria, are the most comprehensive list of toxicity indicators available.[11] MATE's were developed specifically for those species expected to have a potential for forming in combustion processes. They have been developed by experts using the available data and can be compared directly with calculated effluent concentrations of potential pollutants. Although the level of confidence to be associated with MATE's is admittedly imprecise, they have been accepted by EPA for use in Source Analysis Models (SAM's) and can be readily applied to worst case analysis results, with the only difference being that calculated effluent concentrations rather than concentrations based on sampling and analysis results are used.

A worst case effluent concentration-to-MATE ratio is determined for each potential pollutant; organics and inorganics, in elemental and compound form, and in each media. Pollutants are then ranked according to their concentration/MATE ratios, from high to low. Any pollutant with a ratio greater than one is given highest priority and must be considered in the practical analysis which follows. In the lime scrubbing example, roughly half of the potential inorganic pollutants to air had a ratio greater than one. Ratios ranged from 9.17×10^5 (ozone) to 6×10^{-5} (cesium). Ozone is an example of the unrealistic results of worst case analyses. In an actual lime scrubber effluent, the oxygen will exist as mostly water vapor and oxides of sulfur, nitrogen, and trace metals, with very little or none, as O_3. Of course, the worst case analysis also includes the greatest possible concentrations of those oxides and water vapor formed.

In the lime scrubbing worst case analysis, MATE values have not yet been developed for many of the potential pollutants. These potential pollutants could not be ranked with those for which MATE's had been established but were set aside. These potential problems should be considered in the practical analysis.

Once preliminary prioritization has been completed, practical prioritization can begin. The first step is to perform an overall material balance for inlet and outlet streams. Previous experimental results and operating data can be used to determine the distribution of major constitutents between effluent streams. Thermodynamic and kinetic data can be used to predict the formation of trace pollutants in the combustor, given combustor inlet stream compositions. Catalytic plans to use a computer program based on thermodynamic equilibrium calculations to determine the formation of pollutants in a residual oil burner.

The computer program predictions will not be absolutely accurate, since kinetic phenomena such as residence times and rates of formation are not considered; but, the equilibrium calculations are the best projection on which to base the engineering analysis. The species to be considered are limited by the availability of thermodynamic data, but the program will yield results on the inorganics of interest and some of the organics (presently two dozen species).

A practical engineering analysis, including use of computerized equilibrium calculations, if applicable, will yield the expected distribution of trace pollutants between effluent streams, i.e., air, water, and land. Priority I pollutants need to be considered first in the practical analysis. These probable effluent concentrations can then be ranked by MATE ratios, just as the worst case values are.

The result of prioritization is a list of pollutants in order of relative hazard to health and/or ecology. Preliminary or worst case prioritization does not reflect existing control technology. Practical prioritization does reflect existing control technology and indicates the pollutants for which new control methods are needed.

Prioritization is important to EPA because it indicates potential needs for further research and development. Prioritization saves time and money by indicating which pollutants to study first and does so in a much more cost-effective manner than actual sampling and analysis. In most cases, an engineering analysis for a specific set of conditions can be performed in a fraction of the time it would take to obtain samples at those particular conditions. Level 1 sampling and analysis often indicate only a general class of compounds present in a stream, but a thorough engineering analysis (paper study) can determine the probable specific pollutant compounds within that class of compounds. Engineering analysis can often resolve discrepancies between conflicting results in separate sets of sampling data. Practical prioritization results can be more reliable than sampling data due to the potential for human error in sampling and analysis and the possibility of faulty data due to varying process operating conditions. As an indicator of expected results, practical prioritization can point out areas of faulty data and indicate the need for additional sampling.

There are, however, uncertainties in the reliability of prioritization results which arise from uncertainties in the data on which prioritization is based. The uncertainty in the level of confidence associated with MATE's results from uncertainties in health/ecological data and from the lack of consideration of additive, synergistic, and antagonistic effects, as well as the arbitrary assumptions involved in some of the MATE derivations. The lack of thermodynamic and kinetic information on non-equilibrium processes, as well as the shortage of basic thermodynamic data for organic compounds, also contributes to uncertainty in prioritization results. Also, variations in feedstock analyses and process parameters make generalization from specific studies difficult.

Figure 1-1 indicates that pollutant prioritization is a part of environmental objectives development. The preliminary, worst case, prioritization belongs under environmental objectives development as a direct input to environmental data acquisition, where practical prioritization is carried out as part of the comprehensive waste stream characterization and input/output materials characterization. Practical prioritization places emphasis on emissions loadings, determined by material balances and thermodynamic calculations and integrated with sampling results.

Environmental objectives development and environmental data acquisition, which receive direct input from prioritization, are two of the six major components of environmental assessment. Figure 1-1 illustrates the input of environmental assessment into control technology development and vice versa. Environmental assessment determines the need for pollution control via the environmental alternatives analyses, which feeds directly into control technology development, where specific processes are developed and evaluated. The results of control technology development are fed back into the control technology assessment task of environmental assessment.

6.3 STANDARDS SUPPORT PLAN

At the present time, the concept of a Standards Support Plan (SSP) is being implemented on specific energy technologies by several of EPA's Industrial Environmental Research Laboratory contractors. The aim of this effort is to increase the support to the EPA program offices in the area of standards development. In the future, the SSP for residual oil utilization will define the activities and schedules for multimedia assessment efforts on advanced oil processing that relate to standards development. Special reporting formats will be developed by EPA to conform with the requirements for standards setting. A series of environmental assessment reports will then be prepared for key technologies. Thereafter, periodic revisions would be made to reflect changes in policies or technology developments.

The Environmental Assessment Reports (EAR) will summarize background information on the processes, waste streams, control alternatives, environmental impacts, and R&D needs. Separate reports will be prepared for advanced oil processing systems covered in the SSP. For example, environmental assessment reports should be prepared for hydrodesulfurization, and the chemically active fluid bed process, at a minimum. Future environmental assessment reports may also be needed for partial oxidation.

SECTION 7

TECHNOLOGY TRANSFER

Catalytic, Inc. has provided general support and coordination to this environmental assessment program by being a participant in several areas of technology transfer during the past year. Various presentations have been made with the permission of EPA on the status of this program for other government contractors, for process licensors with which Catalytic has entered into secrecy agreements, for CAFB contractors meetings, and for technical societies. The following paragraphs include the types of technology transfers in which Catalytic has participated.

TECHNOLOGY TRANSFER MEETINGS AND ACTIVITIES

To keep abreast of related research and development efforts, Catalytic attended the Second National Conference on the Interagency Energy/Environment sponsored by EPA in Washington, D. C. The broad topics discussed were: fuel processing, utility and industrial power, extraction and benefication, integrated technology assessment, health effects, atmospheric transport and fate, measurement and monitoring, and ecological effects.

During the year, a task leader attended the Fourth FGD Symposium sponsored by EPA. Contractors' reports were assembled in our filing system, and this meeting provided a review and update of the latest FGD methods and control technology problems.

Last Fall, the entire Catalytic task work team attended the EPA-sponsored Contractors' Meeting on Environmental Assessment Methodology Development. Contractors' reports of interest included Level 1 Sampling and Analysis and Bioassays, Level 2 Organic and Inorganic Analysis, Standards of Practice Manual Outline, Source Analysis Models, and Source Assessment Methodology. This meeting provided a review and update of the EPA's environmental assessment methods and problems.

One task leader attended The Second Pacific Chemical Engineering Congress, an international exchange of information from Japan, Mexico, and other Pacific Ocean neighbors. He gathered data on SO_2 stack gas scrubbing technology, environmental control technologies, and system designs of several flue gas desulfurization units. This was an excellent opportunity to update annually both FGD, HDS, and partial oxidation technologies for the residual oil utilization work plan.

In September, 1977, the project manager and a team member attended the IERL/RTP-sponsored Symposium on Environmental Aspects of Fuel Conversion Technology III in Hollywood, Florida. Of particular interest were R. P. Hangebrauck's presentation on Environmental Assessment Methodology and RTI's presentation by Ms. Kingsbury on Multimedia Environmental Goals. Other presentations relevant to Catalytic's environmental assessment work concerned testing, sampling, and analysis of fuel conversion systems and their emissions.

Catalytic, Inc. was given permission by the EPA to make a report at the fall meeting of the Carolinas Air Pollution Control Association (CAPCA). A review of the environmental assessment methodology for residual oil processes was presented. The technical matter presented was well received due to its applicability to any energy fuel process.

Three task leaders attended the Atlanta Process Measurements Symposium sponsored by Environmental Research Laboratory of Research Triangle Park. It was beneficial in defining specific approaches to sampling and analyzing multimedia effluents specifically applicable to our residual oil usage project. The program speakers defined uses of environmental assessment data, the techniques for acquiring data, and users' field experiences, including unsolved problems for future research in environmental assessment measurement programs useful in our residual oil usage program. Of most specific benefit to our project were the field experiences presented by J. W. Hammersma on the "Process Measurements of Conventional Combustion Systems," whereby a number of sampling and analysis exclusion criteria were presented that eliminated wasteful expenditure of funds on unnecessary, existing, available, and unacceptable emission data.

A meeting was held with Dr. W. E. Thompson of Research Triangle Institute to discuss Catalytic's input into their survey of conventional Combustion

Pollutant Assessment (CPA) activities. Dr. Thompson spent one day interviewing members of this project team to summarize our various project objectives and current functional activities using a coded computer technique. These CPA activities will be reported to EPA.

An exchange of information has been initiated with the Technology Division of GCA Corporation to develop meaningful test protocol based upon data previously gathered in Japan and Level 1 sampling experience. Data needs and various aspects of Level 1 sampling and analysis were partially defined during September 1977.

The Volatile Organic Compounds (VOC) are under study for proper sampling and analysis prior to review and coordination with EPA Process Measurements Branch. The sampling program in Japan is anticipated to commence in the Fall of 1978. This program is being coordinated with Dr. Ando.

Proposed New Source Performance Standards for Stationary Gas Turbines were received and reviewed. Modifications were noted to the procedures for sampling and NO_x determination for gas turbines and combined cycles. Our comments were submitted to the appropriate EPA project director.

A draft "Summary of Key Federal Regulations and Criteria for Multimedia Environmental Control" by RTI (dated February, 1977) was received for our use to prevent delays in our prioritization procedures.[11] Also, a draft on "Approach to Level 2 Analysis Based on Level 1 Results, MEG Categories and Compounds and Decision Criteria" was received to aid in the prioritization procedures.[6] Another draft report, "Minimum Acute Toxicity Effluent (MATE) Values for Organic and Inorganic Compounds from Fossil Energy Processes," was received to help in the developing of methodology for setting health/ecological effects objectives.[16]

Another draft report dated 17 August 1977, "Tabulations of Minimum Acute Toxicity Effluent (MATE) Values for Organic and Inorganic Compounds From Fossil Energy Processes," was received to help in the developing of methodology for setting health/ecological effects objectives.

An Aerotherm Project 7250 report entitled "SAM/1A" A Rapid Screening Method for Environmental Assessment of Fossil Energy Process Effluents" was received to aid in the standardization of the environmental assessment system of environmental alternatives analyses procedures encompassing SAM/MEG/MATE system formats.

Since mid-May of 1977, 347 items have been added to Catalytic's information storage and retrieval system. A new system for abstracting and coding has been implemented to improve information retrieval. The total number of items now included in the system is 763.

SECTION 8

FUTURE EFFORTS

Additional research is needed to insure the assessment of present control technology now demonstrated and to determine the best available practices and processes for the effective control of multimedia pollution from residual oil usage. The results of this work will help to identify those areas requiring more research and development.

Sufficient information should be generated to completely characterize effluents and emissions from all processes of interests and their associated control operations. The information is needed to provide the basis for new or revised pollutions standards, as well as for engineering design and economic evaluation of pollution abatement.

It has been known for some time that data deficiency hampers plant design, and scale-up problems hinder the construction of commercial units. The lack of data is even more severe in the area of separation technology, which is the backbone of most pollution control operations. The unavailable data must be developed to overcome the obstacles. These include development of fundamental data in high-temperature and high-pressure operations involving polynuclear aromatic derivatives and the prevalence of H_2, H_2S, CO, CO_2, NH_3, COS, HCN, and H_2O in products of coal gasification and residual oil utilization. Thermodynamic and transport properties of key organic compounds and compounds containing nitrogen, sulfur, and oxygen are urgently needed. Phase equilibria in mixtures containing water, oil, and raw gas are also needed to facilitate engineering design. Compounds derived from many trace metals in coal and residual oil are of particular interest regarding the toxicity and control technology.

For primary process unit operations such as distillation, design to within 5% is considered routine; but, in the separations field, a factor of two is not uncommon. Reliable methods of calculation are needed to solve problems of important practical interest in the physical separation of heterogeneous mixtures, such as cake filtration, granular bed and cartridge filtration, centrifugation, dust collection, cycloning, scrubbing, electrostatic precipitation, thickening, flocculation, and deliquoring of cakes.

Residual oil utilization processes which have high potential for commercialization include regenerable FGD (e.g., double-alkali process and Wellman-Lord process), H-oil hydrodesulfurization process, Eureka or Dow's new steam cracking process, and Exxon's flexicoking gasification process. The engineering and economic evaluation shall include these high-potential processes in the next phase of environmental assessment work.

One goal of the environmental assessment of these processes is to quantify aspects such as economics, energy efficiency, applicability, and environmental impact, so that the processes can be accurately compared. The processes being considered fall into three major categories: pre-treatment, post-combustion treatment, and gasification; but, there are considerable differences to be reviewed and gathered together into a common basis for comparison.

As examples of the process diversity, the process output can be considered. HDS produces a low sulfur fuel oil, while CAFB and POX produce low-Btu gases. Both FGD systems clean up a sulfur dioxide-containing flue gas. Considerable amounts of water are required for both FGD systems with less being consumed in the HDS and CAFB processes (including steam), and essentially none in the POX system. Make-up requirements are relatively simple for the limestone FGD (limestone, water, and fuel oil for reheat), MgO FGD (magnesia, water, and coke), POX (air), and CAFB (air, coal, and steam); but, a large hydrogen plant is required for the HDS process. The quality of the resid feedstock has little effect on the FGD systems, but high metals concentrations can substantially alter the economic favorability of the HDS and POX systems.

The application of SAM/1A methodology and planned sampling of these different processes will be the major segment of the completed environmental assessment. A completed economic analysis and energy efficiency analysis will complement the environmental assessment and process comparison.

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GLOSSARY

ambient level goals: Levels of contaminants in air, water, or land which will not adversely affect human health or the ecology, continuous exposure assumed.

amine regenerator: A process unit which separates amine from the hydrogen sulfide which it has absorbed from the HDS recycle gas.

APTIC: Air Pollution Technical Information Center.

BOD (Biochemical Oxygen Demand): The oxygen required to meet the metabolic needs of aerobic microorganisms in water rich in organic matter; most often used to measure the amount of organic matter in wastewater.

calciner: A unit for heating a material (such as lime) to a high temperature but without fusing in order to drive off volatile matter or to effect changes (as oxidation or pulverization).

capability charge (or demand charge): In the derivation of annual owning and operating costs for an FGD system, both an energy charge (operating cost) and a demand charge (fixed or annual owning cost) can be figured. The demand charge (in dollars per kilowatt) represents the cost of the portion of the total installed capacity which is used by the FGD system. This demand charge is typically 70% of the total power plant installed cost (dollars per kilowatt).

capacity factor: For power generation units, the ratio of total hours in which the unit is generating power divided by the total hours in a year.

chemically active fluid bed: A process for producing a clean gaseous fuel from high sulfur feedstocks by partially combusting the feedstock in a fluid bed (usually limestone) which reacts with and retains the sulfur in the feedstock.

Chilton method: A method which uses multiplication factors for the approximation of direct costs; more detailed and accurate than the Lang method.

Chiyoda: As used here, a process which treats the tail gas from a Claus unit.

Claus: A process which converts H_2S or mixtures of H_2S and SO_2 to elemental sulfur.

COD (Chemical Oxygen Demand): The oxygen equivalent of any organic matter subject to oxidation by a strong chemical oxidant; used as a measurement of organic pollution in wastewater.

DCF (Discounted Cash Flow): A method of profitability evaluation where the time value of money is considered and a rate of return is determined which can be applied to yearly cash flow so that the original investment is reduced to zero during the project life.

degree of hazard: A dimensionless value formed by dividing the MATE value for a given compound or element into the measured or predicted concentration of the compound or element in an effluent stream.

DO (Dissolved Oxygen): The concentration of dissolved oxygen in water, usually expressed in parts per million percentage of saturation.

EAR (Environmental Assessment Reports): A part of the SSP which summarizes background information, waste streams, control alternatives, environmental impact, and R&D needs for specific processes.

effluent gas: A gaseous waste stream leaving any vessel or process and entering the surrounding media.

effluent stream: Waste discharge material leaving any vessel or process and entering the surrounding media.

emission level goals: Desired levels or contaminants in emissions or effluents from a point source.

emissions loadings: The concentrations of particular pollutants of concern in a given effluent stream.

flue gas desulfurization: A process which removes sulfur-containing pollutants from a flue gas stream via contact with an absorbent slurry (such as limestone or MgO).

fractionation: The separation of a mixture into components by partial vaporization and subsequent condensation.

fugitive emissions: Undesirable, uncontrolled non-point source emissions or effluents.

hydrocracking: A catalytic, high-pressure petroleum refinery process that involves the adding of hydrogen to petroleum-derived molecules too massive and complex for gasoline, followed by the cracking of them to the required fuels, the catalyst is an acidic solid and a hydrogenating metal component.

hydrodenitrogenation: The catalytic reduction of organo-nitrogen compounds to NH_3 and low sulfur fuel oil by reaction with hydrogen; occurs along with desulfurization in the HDS process.

GLOSSARY (continued)

hydrodesulfurization: A catalytic process in which the petroleum feedstock is reacted with hydrogen to reduce the sulfur content of the oil by reducing the organo-sulfur compounds to H_2S and low sulfur fuel oil.

IFP (Institut Francais dePetrole): As used here, a process which treats the tail-gas from a Claus unit.

Lang method: A method which uses multiplication factors for the approximation of direct costs.

LC_{50}: The calculated concentration of a substance in either air or water (as separate figures) which will cause the death of 50 percent of an experimental animal population under controlled conditions and time exposure, most often 96 hours for aquatic species.

LD_{20}: The lethal dose to 20 percent of a population (see LD_{50}).

LD_{50}: The lethal dose to 50 percent of a population; the calculated dose of a chemical substance which is expected to cause the death of 50 percent of an entire population of an experimental animal species as determined from exposure to the substance by any route other than inhalation.

Level 1, Level 2, Level 3: The Process Measurements Branch of IERL/RTP has developed and recommended the implementation of a phased sampling and analytical strategy for Environmental Assessment programs. The first phase, Level 1, has as its goal the quantification of mass emissions within a factor of 2 to 3 for inorganic elements and organic classes. The second phase, Level 2, has as its goal the quantification and identification of specific compounds. The third phase, Level 3, has as its goal the continuous monitoring of indicator compounds as surrogates for a large number of specific compounds.

Lurgi process: A fixed-bed coal gasification process.

MATE's (Minimum Acute Toxicity Effluents): The concentration levels of contaminants in air, water, or solid waste effluents that will not evoke significant harmful responses in exposed humans or the ecology, provided the exposure is of limited duration (less than 8 hours per day).

MEG's (Multimedia Environmental Goals): Levels of significant contaminants or degradents (in ambient air, water, or land or in emissions or effluents conveyed to the ambient media) that are judged to be: (1) appropriate for preventing certain negative effects in the surrounding populations or ecosystems; or (2) representative of the control limits achievable through technology.

naphtha: Petroleum fraction with volatility between gasoline and kerosene; used as a gasoline ingredient, solvent for paints and rubber, and cleaning solvent.

GLOSSARY (continued)

NIOSH: National Institute for Occupational Safety and Health.

NTIS: National Technical Information Service.

partial oxidation: Partial combustion of a solid, liquid, or gaseous fuel, in which the degree of combustion is controlled by the amount of combustion air. The products of partial oxidation can be oxidized further to complete the combustion.

particulate: Any solid matter, as opposed to a liquid, which is dispersed in a gas.

pelletizing system: In the POX process, a system which recovers carbon by agglomeration of the soot with a distillate or residual oil, and subsequent separation from the water slurry.

POT (Payout Time): A method of profitability evaluation which determines the minimum length of time theoretically necessary to recover the original capital investment in the form of cash flow.

quench gas: A gas used to control (decrease) the temperature of segments of a reactor.

recycle gas: Recoverable fraction of a process product gas stream which is often used as a quench gas or mixed with the feed stream.

residual fuel oil: Combustible, viscous, or semi-liquid petroleum product remaining after refinery separation of light fractions of crude oil; high in sulfur ash and heavy metal content.

residual oil gasification: A general term for any of several processes (such as POX or CAFB) by which a liquid residual oil feedstock is partially combusted to generate a product gas suitable for use in power generation via a boiler or gas turbine.

RESOX: A process which converts dilute SO_2 from a gas stream into elemental sulfur.

ROI (Return on Investment): A method of profitability evaluation in which the expected profit is divided by the total initial investment.

SAD: Source Assessment Document.

SAM: Source Analysis Model.

SAM/1A: A rapid screening method for environmental assessment of fossil energy process effluents.

SASS: Source Assessment Sampling System.

GLOSSARY (continued)

SCOT (Shell Claus Off-Gas Treatment) unit: A system used to clean up any residual H_2S or SO_2 emission gas leaving the Claus unit that converts gases into elemental sulfur.

SELEXOL: Low temperature gas cleanup process using polyethylene glycol ether as a physical solvent type of absorbent that selectively absorbs hydrogen sulfide and carbonyl sulfide.

sludge: Residue left after acid treatment of petroleum oils. Any semi-solid waste from a chemical process.

slurry: A free-flowing, pumpable suspension of fine solid material in liquid.

sour fuel gas: Natural gas or synthesis gas that contains corrosive, sulfur-bearing compounds, such as hydrogen sulfide and mercaptans.

SSP: Standards Support Plan.

STOREX: A computer information pollution data retrieval system for various chemical processes located at some specific site.

Stretford: A low-temperature gas cleanup process using sodium carbonate and anthraquinone sulfonic acid to direct converted hydrogen sulfide into elemental sulfur.

synthesis gas: A mixture of gases prepared as feedstock for a chemical reaction; for example, carbon monoxide and hydrogen to make hydrocarbons or organic chemicals or hydrogen and nitrogen to make ammonia.

tail gas treater: Can imply the use of any FGD system or a flare stack incinerator system for absorption or burning of residual emissions gases.

TD_{Lo} (Lowest Toxic Dose): The lowest dose reported to induce carcinogenic, teratogenic, or other toxic effects in humans or animals when introduced by any route other than inhalation.

TDS (Total Dissolved Solids): Quantitative analysis value for measuring water quality.

TLM (TLm) (Medium Tolerance Limit): This measure of aquatic toxicity means that approximately 50 percent of the fish will die under the conditions of concentration and time given.

TSS (Total Suspended Solids): The total content of suspended and dissolved solids in water.

UAC: Uniform Annual Cost.

unit process modules: A detailed definition of a basic control technology process subdivided into control/disposal options for gaseous emissions, wastewater effluents, and solid waste disposal methods.

venturi scrubber (Chem. Eng.): A gas-cleaning device in which liquid injected at the throat of a venturi is used to scrub dust and mist from the gas flowing through the venturi.

volatilization: The conversion of a chemical substance from a liquid or solid state to a gaseous or vapor state by the application of heat, by reducing pressure, or by a combination of these processes. Also known as vaporization.

Wellman-Lord sodium sulfite scrubbing process: A process used to remove sulfur dioxide from flue gases by absorption.

WRA: Water Resource Abstracts.